ENERGY, MINES AND RESOURCES CANADA

CANMET

NEW TECHNOLOGY APPRAISAL OF LEAD CHLORIDE ELECTROLYSIS AND CONCEPTUAL DESIGN OF A CELL

ENERGY, MINES AND RESOURCES CANADA

THE CANADA CENTRE

FOR MINERAL AND ENERGY TECHNOLOGY

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NEW TECHNOLOGY APPRAISAL OF LEAD CHLORIDE ELECTROLYSIS AND CONCEPTUAL DESIGN OF A CELL

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EXECUTIVE SUMMARY/
SOMMAIRE

EXECUTIVE SUMMARY

The potential of producing lead, and other base metals, from sulphide concentrates or ores, in a chloride medium has been under consideration for several decades. Since the sulphur dioxide emission from non-ferrous metals smelters became an environmental issue and as the search for technically and economically feasible processes to treat complex base metal ores has been intensified, the interest in trying to develop processes based on chloride leach/electrolysis has increased.

CANMET has been involved in these activities and has been developing a chloride-based leach/electrolysis process producing lead, as well as zinc, silver and copper, from various grades of sulphide concentrates. SNC has also been interested in these developments and CANMET accepted a proposal submitted by SNC to carry out this study involving a technical review of the state-of-the-art of the development of fused salt and aqueous electrolysis methods for producing lead from lead chloride produced by the ferric chloride leaching of sulphide concentrates, a comparison of these electrolysis processes, a conceptual design for a pilot plant scale cell, and formulation of guidelines for future work.

The review is based on information compiled during visits to the selected research centers and production facilities, and on published data. The review includes eight fused salt electrolysis, ten aqueous electrolysis and four other related technologies.

It is concluded that the technical feasibility of the production of lead from lead chloride crystals or solution by fused salt or aqueous electrolysis has been proven in pilot scale operations. However, the economic viability of these processes has yet to be proven, and this makes a confident selection of an electrolysis technology to be adopted for a pilot scale test program difficult.

In both types of electrolysis, the purity of the lead produced is dependent on the purity of the lead chloride, and the crystallization stage is the key to the production of high purity lead chloride.

Among the processes reviewed, the USBM process, the Alcoa Smelting Process, the Minemet Recherche Process and the Boliden/Dextec Electrowinning Cell technologies have been identified as being the most advanced. After a test program, it would be possible to build commercial scale plants based on these technologies.

It is recommended that CANMET should prove the technical feasibility of the entire two-stage ferric chloride leaching process, while simultaneously carrying out a cost comparison between the advanced electrolysis processes and the existing pyrometallurgical processes, to determine accurately the most economically viable route. If a pilot scale testing facility were to be set up in the near future, it is recommended to adopt one of the cell technologies developed by others. Accordingly, the USBM process was selected and a conceptual design of a 10,000 ampere cell was prepared.

SOMMAIRE

Depuis plusieurs décennies, on étudie la possibilité de produire du plomb et d'autres métaux communs à partir de concentrés ou de minerais sulfureux, à l'aide d'un procédé reposant sur leurs chlorures. Comme l'émission d'anhydride sulfureux, par les fonderies de métaux non ferreux, est devenue un problème d'environnement, et comme, d'autre part, la recherche de procédés techniquement et économiquement valables s'est intensifiée dans le but de traiter les minerais complexes, on voit l'intérêt croître à l'égard des possiblités de procédés reposant sur la lixiviation et sur l'électrolyse des chlorures.

CANMET participe à ces études et recherches, et a mis au point un procédé de lixiviation-électrolyse de chlorure pour produire du plomb, ainsi que du zinc, de l'argent et du cuivre à partir de divers concentrés sulfureux. Le Groupe SNC s'intéresse également à ces développements et CANMET a accepté la proposition du Groupe d'effectuer la présente étude qui comporte l'examen technique de l'état actuel des méthodes d'électrolyse en bain aqueux ou en bain de sel, pour produire du plomb à partir de chlorure de plomb obtenu par la lixivation de concentrés sulfureux par du chlorure ferrique; l'étude comprend aussi une comparaison de ces procédés d'électrolyse, un projet de conception de cuve à l'échelle d'une usine pilote, et la formulation de directives pour les travaux à venir.

L'examen technique repose sur les renseignements compilés au cours de visites effectuées dans des centres de recherche et des installations de production, ainsi que sur les données publiées. Il passe en revue huit technologies d'électrolyse en bain de sel, dix d'électrolyse en bain aqueux et quatre technologies connexes.

On a donc pu conclure que la faisabilité technique de la production de plomb à partir de cristaux ou d'une solution de chlorure de plomb, par électrolyse en bain de sel ou en bain aqueux, a été démontrée à l'échelle de la production pilote. Cependant, la viabilité économique de ces procédés reste encore à prouver, et ceci rend difficile la sélection d'une technologie d'électrolyse pour un programme d'essais à l'échelle pilote.

Dans les deux méthodes d'électrolyse, la pureté du plomb obtenu dépend de celle du chlorure de plomb et l'étape de cristallisation est déterminante pour obtenir du chlorure de plomb pur.

Parmi les procédés décrits, le procédé USBM, le procédé de fusion Alcoa, le procédé Minemet Recherche et les technologies d'électro-concentration en cuve de Boliden/Dextec ont été identifés comme étant les plus avancés. A l'issue d'un programme d'essais, il serait possible de construire des usines, à l'échelle commerciale, faisant appel à ces technologies.

SOMMAIRE (suite)

Il est recommandé à CANMET de s'employer à démontrer la faisabilité technique de l'ensemble du procédé de lixiviation par chlorure ferrique en deux étapes, tout en effectuant une comparaison économique entre les procédés d'électrolyse avancés et les procédés pyro-métallurgiques plus conventionnels, afin de déterminer avec précision l'orientation qui serait la plus viable économiquement. Si une installation d'essai pilote doit être créée dans un avenir proche, il est recommandé d'adopter l'une des technologies d'électrolyse mises au point ailleurs. On a donc choisi le procédé USBM dans ce but et une étude d'un projet de cuve de 10 000 ampères a été préparé.

1.0 INTRODUCTION

1.0 INTRODUCTION

This report presents a technical review of the state-of-the-art of the development of fused salt and aqueous electrolysis methods for producing lead from lead chloride produced by the ferric chloride leaching of sulphide concentrates. It also makes a comparison of these electrolysis processes, gives a conceptual design for a pilot plant scale 10,000 A cell for fused salt electrolysis and presents guidelines for future work.

SNC has long been involved with the environmental concerns surrounding non-ferrous metals smelters treating sulphide concentrates, in seeking ways of reducing sulphur dioxide emissions, and the treatment of complex sulphide concentrates. Through this involvement, SNC became aware of the research being carried out during the last decade in Canada, the U.S.A. and other parts of the world on the production of lead from its sulphide concentrates by a chloride-based leach/electrolysis process which can eliminate production of sulphur dioxide completely. Knowing the research which has been carried out at CANMET in this field, at a meeting held in November 1984, the SNC interest in the development of this new process was expressed to Dr. J.E. Dutrizac of CANMET.

As a result of that meeting and based on ensuing discussions held with CANMET staff in February 1985, SNC submitted a proposal in March 1985 for consulting services to carry out an independent technical/economic evaluation of lead production through electrolysis of lead chloride fused salt melts or aqueous solutions, to prepare a conceptual design for a cell for aqueous or fused salt electrolysis and to establish guidelines for further development and pilot plant scale test work. The intent was to establish an electrolysis process to complement the process of ferric chloride leaching of concentrates containing lead sulphide that has been developed by CANMET.

The proposal was accepted and approved in October 1985 and the implementation of the study was started in November 1985. In accordance with the scope of services, visits and meetings with selected scientists and companies who are carrying out research in base and light metals chloride electrolysis pertinent to the lead chloride electrolysis were carried out until June 1986. During these visits, information was collected using a questionnaire prepared by SNC. Simultaneously, a literature review was carried out. The literature review was based on publications in the possession of SNC and CANMET, and a computer survey carried out through the SNC library.

In addition to the review discussions held with the Scientific Authority on various occasions during the visits to the other scientists, progress review meetings were held in July 1986 and February 1987 at the SNC offices.

1.0 INTRODUCTION (Cont'd)

In January 1987, an Interim Report which included the results of the review of technologies and the comparison between fused salt electrolysis and aqueous electrolysis was issued to CANMET. Comments of the Scientific Authority were received and are incorporated in the final report. As part of the Confidentiality Agreement signed with the companies visited during the review, pertinent sections of the Interim Report were sent to these companies and their consents and comments were obtained. At the same time, a conceptual design was prepared for a 10,000 A fused salt electrolysis cell as a result of decision made in coordination with the Scientific Authority. Subsequently, guidelines for future work were established.

In Section 2 of this report, the methodology used for collecting the information on the technologies is described briefly. Section 3 contains the review of the electrolysis technologies which were considered relevant to lead chloride electrolysis. In Section 4, results of a comparison of fused salt electrolysis with aqueous electrolysis are listed and Section 5 includes the conceptual cell design and guidelines for future work. Sections 6 and 7 include the conclusions and recommendations, and the acknowledgements, respectively. In Section 8, references used for the review of the processes are listed.

2.0 COLLECTION OF INFORMATION ON THE TECHNOLOGIES

2.0 COLLECTION OF INFORMATION ON THE TECHNOLOGIES

2.1 General

Information on the research and development which have been carried out on the electrolysis of lead chloride in fused salt or aqueous solution was collected by:

- visiting selected research centers and production facilities
- reviewing publications in the possession of SNC and CANMET, and
- carrying out a computerized literature survey through the library of SNC.

2.2 Visits to Selected Research Centers and Production Facilities

The visits to the selected research centers and production facilities were carried out intermittently from November 1985 through May 1986. The Scientific Authority of CANMET accompanied the SNC Study Manager during the visits made in November 1985, and January and April 1986. Another CANMET senior officer, W.J.S. Craigen, accompanied the SNC Study Manager for the visits made in May 1986.

A list of the research centers and the production facilities to be visited was included in the study scope of services by SNC. This list was reviewed with the Scientific Authority of CANMET and some changes were made. The selection was made based on two major factors: a) the degree of relevance of the research and development work and b) the stage of the research and development work, with pilot plant and commercial scale operations being favoured.

Among the research centers and production facilities which were contacted, Falconbridge Nikkelverk, Kristiansand, Norway and Société Metallurgique de Nickel of France rejected the SNC request for permission to visit their facilities because of a reluctance to disclose know-how regarding their chloride technologies.

Prior to the visits, a questionnaire was prepared by SNC to facilitate the systematic collection of data. It was also used as a guide for discussions during the visits.

The following visits were made:

November 1985 - St. Joe Minerals Corp., Pittsburgh, Pennsylvania
- Alcoa Research Center, Alcoa Center, Pennsylvania

2.2 Visits to Selected Research Centers and Production Facilities (Cont'd)

January 1986
- U.S.B.M. Reno Research Center, Reno, Nevada
- Hazen Research Inc., Golden, Colorado
- Duval Corporation, Tucson, Arizona
- Alcoa, Anderson County Works, Texas

April 1986
- Minemet Recherche, Trappes, France
- Boliden Metal, Skelleftehamn, Sweden
- Meeting with P.K. Everett of Dextec Metallurgical Pty. Ltd. in Toronto

May 1986
- U.S.B.M. Reno Research Center, Reno, Nevada
- Timet, Henderson, Nevada

During the visits, the Study Manager and the Scientific Authority or the CANMET senior officer held meetings with the scientists who were involved in the research and development work, and whenever possible they toured the facilities where the research was carried out and inspected the equipment.

After each visit, a trip report was prepared. These reports were included in Appendix A of the Interim Report. Questionnaires were filled out for the research and development work carried out by St. Joe Minerals Corp., Alcoa Research Center, U.S.B.M. Reno Research Center, Minemet Recherche, Boliden Metall-Dextec Process and Timet - Alcan-Type Magnesium Cell, and these were included in Appendix B of the Interim Report.

General Comments

St. Joe Minerals Corporation has carried out research and development work with Alcoa, Duval Corporation, Hazen Research Inc., Minemet and U.S.B.M. Reno Research Center in the electrolysis of lead chloride in both fused salt and aqueous solution.

Alcoa Research Center studied fused salt lead chloride electrolysis in the bipolar cell. The technology was originally developed for the production of aluminum and it was proven in a commercial scale prototype plant located in Anderson County, Texas. The applicability of the process to lead production was shown in pilot scale test work done under a contract with St. Joe Minerals Corporation.

2.2 Visits to Selected Research Centers and Production Facilities (Cont'd)

U.S.B.M. Reno Research Center studied lead chloride electrolysis both in fused salt baths and aqueous solution in laboratory scale cells. They then selected fused salt electrolysis in a monopolar cell for study in a pilot scale test program.

Hazen Research Inc. studied the concept of the electrolysis of lead chloride in both fused salt melts and aqueous solution in bench scale tests. Later, they selected a unique process based on hydrogen reduction of lead chloride and built a pilot plant. The process was called the Advanced Mineral Technology Lead Process. After the death of the investor, the project was abandoned.

Duval Corporation has its own patented technology for electrolysis in solution, which has been proven on a commercial scale for copper production. Under a contract with St. Joe Minerals Corporation, the applicability of the process to lead production was investigated in a laboratory scale cell.

Minemet Recherche has its own technology of electrolysis in aqueous solution that has been proven for lead production in a pilot plant scale cell.

Boliden Metal carried out laboratory and pilot plant scale test programs with the Dextec Process for de-leading copper concentrates. The pilot plant was based on a commercial scale cell. The Dextec Process has been developed to treat complex sulphide concentrates, incorporating ferric chloride leaching and electrolysis in one electrolytic cell and selectively producing lead, copper, zinc and silver.

Alcan has electrolysis technology to produce magnesium from magnesium chloride in a fused salt cell. This process was developed in Canada and proven in a commercial scale plant in Arvida. It was then licenced to Osaka Titanium Co. Ltd. in Japan, and to ORMET and TIMET in the U.S.A.

With the exception of the TIMET operations, every research or production facility that was visited had terminated research work in this field. This was due mainly to the general economic situation in the base metals industry and in particular to the relatively low price of lead. Some of the technologies had been developed to a level such that the next stage would have been the building of a prototype commercial scale plant. However, the management of the various companies had decided that economic conditions were not favourable for building a commercial scale plant at that time.

2.3 The Literature Review

Publications available in the SNC and CANMET files were combined and utilized as the basis for the literature review. During the visits to the research centers and the production facilities, reports and articles were received and added to the collection of publications. In addition, a computer survey was carried out through the SNC Library.

The computer survey covered the data banks of the Chemical Abstracts (American Chemical Society - July 1973 through June 1986) and Metals Abstracts (METADEX - 1966 through July 1986).

Some 500 citations were selected and classified according to the languages in which the articles were published and according to the products cited; i.e. lead, copper, nickel, zinc, aluminum, magnesium and other metals.

Citations which related to lead chloride electrolysis, published in English or French, were separated from the list and are included in the Reference List in Section 8.0. Articles on lead chloride electrolysis published in languages other than English or French were not included in the literature review due to the high cost of translation, which was not allowed for in the study budget. However, these citations were listed with the other citations on copper, nickel, zinc, aluminum and magnesium, and all of them were included in Appendix C of the Interim Report as a source of information on the chloride metallurgy of these metals.

3.0 REVIEW OF TECHNOLOGIES

3.0 REVIEW OF TECHNOLOGIES

3.1 General

A review of the electrolysis technologies which were considered relevant to lead chloride electrolysis is presented in this section. For each technology, depending on the amount of information available, a technical/economic appraisal has been prepared including a brief description of the technology, location of the development, its degree of progress/status, its production rate, its physical size, materials of construction of the electrolysis cell, raw materials and energy requirements, other operating parameters, characteristics of the products and by-products, comments on the advantages/disadvantages of the technology, and comments on environmental concerns.

The appraisal of technologies was based on the information collected during the visits to the selected research centers and production facilities, the companies responses to the questionnaire and the published reports and articles.

The published information utilized for preparing this appraisal is listed in Section 8.1. The electrolysis technologies in chloride media which were developed to produce lead from scrap batteries or other lead alloys were not included in the appraisal. However, published information available on these electrolysis processes, leaching processes and other information on the chemistry or thermodynamics of lead production in chloride media are listed in Section 8.2.

3.2 Classification of the Technologies

In this review, technologies are classified into three groups, as follows:

a) Technologies for Fused Salt Electrolysis

- USBM Molten Salt Electrolysis
- Alcoa Smelting Process
- Hazen Research Molten Salt Electrolysis
  - Hazen/Cymet Design
  - Hazen/St. Joe Design
- United Oil Products (UOP) Process
- Cominco Hydrometallurgical Process
- Alcan-Type Magnesium Cell.

3.2 Classification of the Technologies (Cont'd)

b) Technologies for Aqueous Electrolysis

- Minemet Recherche Process
- CLEAR Process
- Cymet Process
- USBM Aqueous Electrolysis Test Work and a Conceptual Design by Hazen
- Amax Test Work
- The Research Group of R. Kammel Test Work
- Elkem Test Work
- Falconbridge Chlorine Leach Process
- SLN Nickel Electrolysis Process
- GCM Hydrometallurgical Copper Process.

c) Other Related Technologies

- Leadex Process
- Boliden/Dextec Electrowinning Cell
- AMT Lead Process (Hazen)
- Hazen Carbon Reduction Process.

The first two groups of technologies are considered as potentially applicable, without major changes, to the lead chloride crystals or solutions which could be produced by the ferric chloride leaching process developed by CANMET. The technologies which would replace the leaching process, or would not require a leaching process, are included under the heading of Other Related Technologies.

3.3 Technologies for Fused Salt Electrolysis

3.3.1 USBM Molten Salt Electrolysis

The Bureau of Mines investigated the ferric chloride leaching of galena followed by both molten salt and aqueous electrolysis of lead from lead chloride. The molten salt electrolysis was selected and a substantial amount of development work has been carried out. (References 1 through 16).

The Bureau of Mines leach-electrolysis process is based on leaching galena concentrate in ferric chloride-sodium chloride solution for about 15 minutes at 90-95°C, during which more than 99% of the lead sulphide is converted to lead chloride. The pulp is then filtered to remove elemental sulphur and gangue. High-purity lead chloride (more than 99.9%) is crystallized from the filtrate on cooling. After drying, the crystals are fed to the molten salt electrolysis cell where lead metal is produced and chlorine gas is generated for recycle.

The research was partly financed by a consortium of lead producing companies including St.Joe Minerals Corp., Asarco, Amax, and Cominco Ltd.

The Bureau of Mines development work included various sizes of cell from bench scale through intermediate and pilot-scale. In the bench scale tests monopolar and bipolar electrodes, different compositions of electrolyte ($PbCl_2$, $LiCl-PbCl_2$, $KCl-PbCl_2$, $NaCl-PbCl_2$, $LiCl-KCl-PbCl_2$ and $NaCl-KCl-PbCl_2$) and various configurations of electrodes were tested. Based on the results of these tests, several cells of intermediate size, 100 to 400 ampere, were built to obtain data for designing larger cells.

Finally, a 3,000 A monopolar cell which was part of a semi-continuous integrated leaching-electrolysis operation, capable of producing 225 kg of lead metal per day, was tested periodically over a period of three years. A schematic diagram of the cell, which was called the process development unit (PDU), is shown in Figures 1.A and 1.B. The cell interior dimensions were 86 cm long, 64 cm wide, and 46 cm deep. The inside walls were constructed of silica brick surrounded by castable refractory and insulating brick. The mild steel lid had a 7.6 cm thick layer of lightweight castable insulation. The cell exterior dimensions were 135 cm long, 112 cm wide and 76 cm high. Two graphite plate anodes, 36 by 60 by 7.6 cm were screwed to two 15 cm diameter graphite rods which were connected to an anode busbar. The

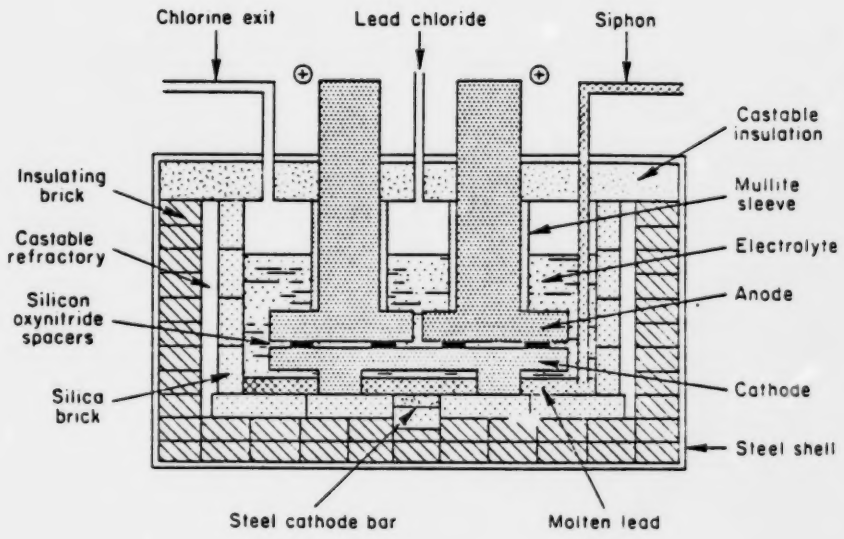


FIGURE 1.A - 3,000 A FUSED SALT CELL DESIGNED BY USBM TO PRODUCE LEAD

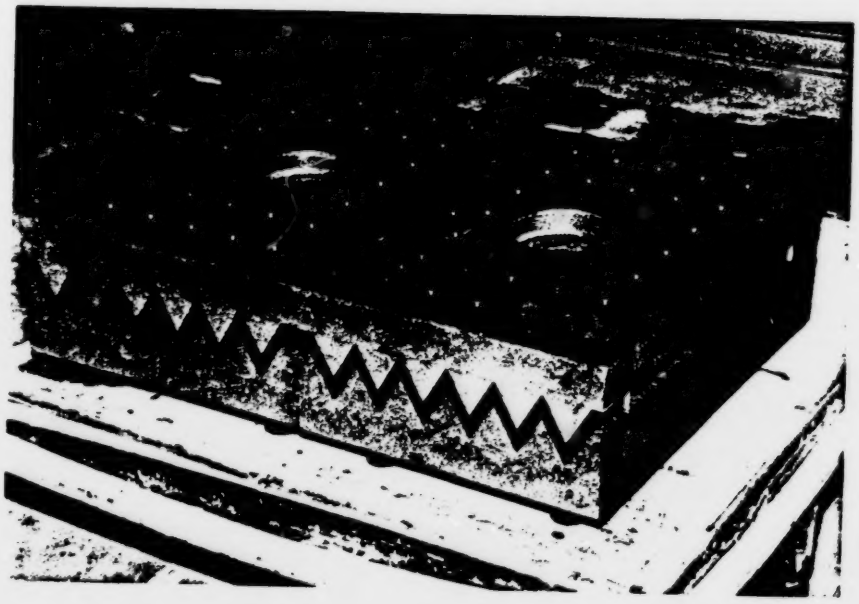


FIGURE 1.B - SAW-TOOTH ELECTRODE DESIGNED BY
USBM FOR FUSED SALT CELL ELECTROLYSIS

3.3.1 USBM Molten Salt Electrolysis (Cont'd)

graphite rods above the anode plates were protected from air oxidation by mullite sleeves. A graphite plate cathode, 74 by 60 by 5 cm, was supported by four 7.6 cm diameter graphite rods which were partially immersed in a pool of molten lead metal and 7.6 cm high from the bottom of the cavity. Under the molten lead metal pool, a 15 cm wide by 5 cm thick steel plate protruding through the bottom of the cell was cathodically connected to a 5,000 A rectifier. The anode plates and the cathode plate were separated by 1.9 cm silicon oxynitride spacers. The surfaces of the anode and cathode plates had six 0.64 cm wide, slanted grooves to channel chlorine and lead metal to the opposite sides of the cell. Lead chloride was added to the cell from a hopper fitted with a screw feeder. The electrolyte composition was 6.5% LiCl, 16.5% KCl and 77% $PbCl_2$ by weight.

The minimum depth of molten lead was kept at 13 mm and the maximum depth was 40 mm. The electrolyte layer was about 200 mm deep.

Lead chloride was added to the cell from the feed hopper by a screw feeder which was controlled by a timer. Chlorine from the exit port was diluted to 30% by volume with air through an adjustable draft outside the cell and drawn through an FRP pipe to the bottom of the chlorination tower. Chlorine from a tank provided a backup source when needed and compensated for the losses of chlorine in the exhaust from the chlorination tower and extraction of metals other than lead in the circuit. Lead metal produced in the electrolytic cell was siphoned through a removable Pyrex tube connecting the cell bottom to a vacuum chamber in which a mould was used to collect the metal. Two auxiliary 7.6 cm diameter graphite electrodes projected through the top of the cell and into the electrolyte to a depth of 5 cm. These electrodes were connected to an AC power supply which kept the electrolyte molten when the cell was not in use. During electrolysis no supplementary heat was required.

Table 1 shows the operating data from start up in November 1978 to April 1980 and average operating data are summarized in Table 2. In the recent experiments with the saw-tooth electrodes, the ampere-hour data were obtained by averaging the output from two Curtis 1002 integrating meters. Voltages were measured with a Fluke Model 8026B multimeter calibrated against a potentiometer. Current was measured with a potentiometer and a calibrated shunt.

TABLE 1 - OPERATING DATA FOR ELECTROWINNING LEAD METAL IN THE 3,000 A CELL DESIGNED BY USBM

	OPERATING PERIOD[1].							
	11/6/78-1/31/79	1/6-15/79	3/13-22/79	6/19-28/79	10/22-26/79	12/3-7/79	1/28-2/1/80	4/1-11/80
Ave. current, A	3,000	2,860	3,570	2,948	2,868	2,365	3,100	3,050
Ave. voltage, V	5.1	4.8	4.3	4.4	4.5	5.2	4.7	4.5
Ave. electrolyte temp., °C	439	453	437	450	457	454	455	454
Ave. lead metal temp., °C	404	434	402	423	434	432	427	432
Ave. anode current density, A/cm^2	0.69	0.66	0.83	0.68	0.66	0.55	0.72	0.71
Ave. cathode current density, A/cm^2	0.68	0.64	0.80	0.66	0.65	0.53	0.70	0.69
Ampere-hours used	483,000	603,500	532,500	597,500	266,343	244,496	277,715	307,145
$PbCl_2$ added, kg	3,108	2,993	2,443	2,864	1,432	1,148	1,309	1,326
Lead produced, kg	1,685	2,140	1,930	2,157	974	856	987	1,108
Current efficiency, %	91	92	94	93	94	90	92	86
Energy requirement, kWh/kg Pb	1.46	1.35	1.19	1.22	1.23	1.49	1.32	1.36

1. Runs were continuous except during the period 11/6/78 - 1/31/79, when the operation was intermittent.

TABLE 2 - AVERAGE OPERATING DATA FOR 3,000 A AND 4,000 A CELLS WITH FLAT PLATE AND SAWTOOTH ELECTRODES, DESIGNED BY USBM TO PRODUCE LEAD

	FLAT PLATE	SAWTOOTH	
Current, A	3,000	3,000	4,000
Voltage, V	4.7	2.5	3.0
Electrolyte temperature, °C	450	450	450
Electrode current density, A/cm^2	0.68	0.36	0.48
Electrode spacing, cm	1.91	1.27	1.27
Current efficiency, %	93	98.7	99.5
Ampere-hours consumed	3,005,064	426,527	230,640
Lead produced, kg	10,740	1,631	886
Energy requirement, kWh/kg Pb	1.32	0.66	0.77
Lead production rate, kg/h	10.0	11.0	15.0

3.3.1 USBM Molten Salt Electrolysis (Cont'd)

The Bureau of Mines stated that the test work with the process development unit (PDU) successfully demonstrated in the early stages that the process produced high purity lead metal with minimum health hazards due to the low operating temperatures (3). The research program continued to improve the electrode assembly design that would increase the rate of chlorine removal from the space between the electrodes while maximizing the effective electrode area, minimizing the interelectrode spacing and ultimately increasing the current efficiency. The impurity control in the electrolyte and the product lead, and the effects of impurity build up in the electrolyte on the current efficiency also were investigated (4).

The electrode assemblies, which were referred to as vertical flat plate, square-wave and sawtooth, were tested on a bench scale cell and the results were compared with the results obtained with the horizontal flat plate assembly (1, 2). Current density-voltage curves were obtained for all electrode designs by increasing the current density incrementally. The lowest voltage requirements were recorded with the vertical plate electrodes followed by the sawtooth, the square-wave, and the horizontal flat-plate assemblies.

The sawtooth electrode design was chosen for scale-up rather than the vertical-plate design. This was due to two reasons stated by the Bureau of Mines (2) a) the electrode assembly had to occupy the same volume in the cell cavity so that the cell would have the same dimensions as the PDU cell and it was considered easier to incorporate the sawtooth electrode design into the cell design, and b) the sawtooth electrodes could be fabricated easily from a block of graphite.

The angles of the triangular cuts in the sawtooth electrodes were 60° which gave the maximum effective electrode area at 13 mm electrode spacing. A picture of the anode is included in Figure 1.B. Series of tests were carried out with the new pilot scale cell incorporating the sawtooth electrodes at 3000A and 4000A. The cell had the identical inside and outside dimensions with the cell in which flat-plate electrodes were tested. The results are included in Table 2 to facilitate the comparison with the flat-plate electrodes. At 3000A, the energy requirement was 50% less than with the flat-plate electrodes. This could be achieved by reducing the electrode spacing, facilitating increased removal of chlorine gas from the anode and doubling the electrode surface area.

3.3.1 USBM Molten Salt Electrolysis (Cont'd)

The effects of impurities on the electrolysis were investigated on both the bench scale and the PDU cells (3, 4). It was shown that the elements which are less noble than lead, such as calcium, sodium, iron, zinc and magnesium, showed a tendency to increase in the electrolyte, and this increased the viscosity of the electrolyte and caused variations in the cell resistance. Copper, iron, calcium and sulphate accumulations in the electrolyte had the most significant effect on the cell resistance.

It was also shown that copper and silver were the only detectable metallic impurities in the lead product. The concentrations of copper and silver in the lead product were directly dependent on their concentrations in the ferric chloride leaching solution. The analysis of the lead product obtained by the Bureau of Mines was (all in parts per million and less than) 3.0 silver, 40.0 copper, 15.0 bismuth, 0.7 calcium, 0.8 cadmium, 2.5 cobalt, 3.0 iron, 2.5 nickel, 25.0 antimony, and 1.0 zinc (3).

The Bureau of Mines stated that they had no problems with the materials of construction of the cell, but it was considered that the graphite cathodes could be a potential problem. They also showed that the technology is environmentally safe.

The research program was terminated in 1985 and the pilot plant was dismantled due to the lack of interest in new investment in the industry as a result of general market conditions. Detailed information on the technology is available in numerous publications and, if needed, the Bureau of Mines is willing to provide more information.

The process has been developed to the stage that a pilot plant unit or a semi-commercial prototype unit could be built which could be incorporated with the leaching process developed by CANMET, in order to fine tune the complete process flowsheet and optimize the operating parameters.

Information on the economics of the process is limited. Two cost estimates have been prepared for the commercial scale plants producing lead and silver (6, 8). However, the information is not adequate to be utilized for carrying out comparison studies with other technologies.

3.3.2 Alcoa Smelting Process

Aluminum Company of America (Alcoa) has developed the Alcoa Smelting Process to produce aluminum as an alternative to the traditional Hall-Heroult Process. It is possible to employ the process for other metals, such as magnesium, zinc or lead. The process is based on converting aluminum oxide to aluminum chloride with carbon and chlorine in a fluid bed reactor and feeding the aluminum chloride to the Alcoa Smelting Process (ASP) bipolar cell where aluminum is produced on the cathode surface and chlorine gas on the anode surface. Chlorine is recycled to the chlorination step.

The process and the equipment have been described in a series of patents which are listed in Section 5.0 (17-42). The cross section of the cell is shown in Figure 2. A commercial scale plant producing 15,000 tonnes aluminum per year was built by Alcoa and operated from June 1976 until June 1982. The plant facilities included materials receiving and handling, chlorination system, eight ASP bipolar cells with total production capacity of 30,000 tonnes aluminum per year, aluminum casting, storage and shipping, and chlorine gas cleaning, handling and storage systems. Due to the general aluminum market conditions, production was stopped in 1982 and in 1986 the plant was being dismantled.

The applicability of the electrolysis process to lead production was demonstrated in a pilot scale test program, a joint effort of Alcoa and St. Joe Minerals Corp.

$PbCl_2$ was produced by St. Joe Minerals Corporation at a ferric chloride leaching pilot plant located in Monaca, Pennsylvania and was shipped to the Alcoa Research Center where the ASP pilot plant was located. The chloride leaching pilot plant of St. Joe Minerals Corp. is described in reference 43. A typical analysis of St. Joe lead chloride is given in Table 3.

The ASP pilot plant treating St. Joe's lead chloride was operated for some six months and about 91 tonnes of high purity lead, equivalent to Doe Run quality, (Table 4) was produced at a rate of 77 kg per hour. Average operating data are listed in Table 5. The bipolar cell had either 6 (20,000 A) or 3 (10,000 A) compartments, the horizontally placed electrodes being in vertical stacks.

The cell was rectangular in shape with inside dimensions of 279 cm deep x 20 cm wide x 191 cm long and outside dimensions of 354 cm deep x 74 cm wide x 245 cm long. The shell was made of mild steel and the lining material was Harbison Walker Duro and HW 30 LI bricks. The electrodes were made of graphite.

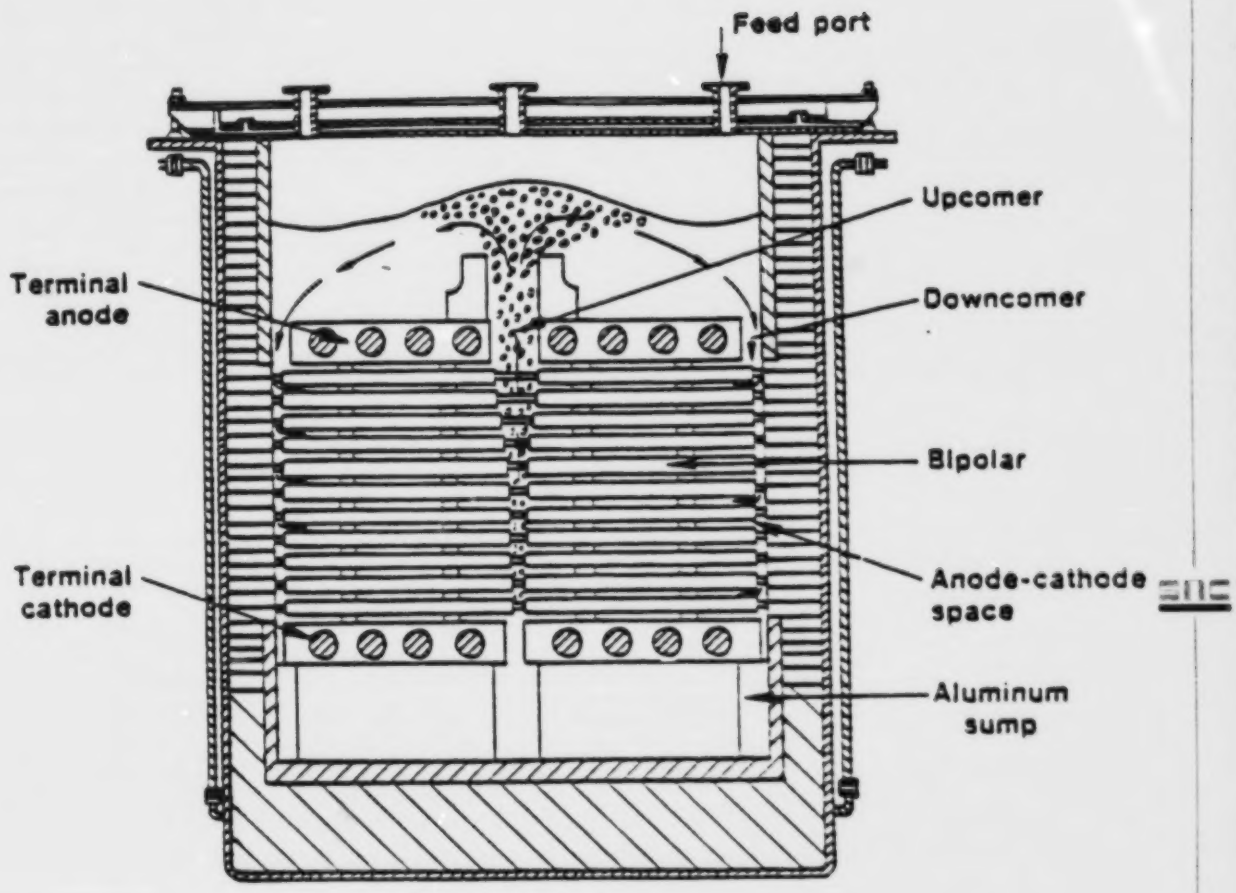


FIGURE 2 THE ALCOA SMELTING PROCESS CELL DESIGNED TO PRODUCE ALUMINUM

TABLE 3 - TYPICAL ANALYSIS OF ST. JOE LEAD CHLORIDE

Element	Concentration, ppm
S	200-500
Na	25-100
Fe	10-40
Zn	2-10
Cu	1-3
Ag	2
$PbCl_2$	Balance

TABLE 4 - TYPICAL ANALYSIS FOR DOE RUN AND CORRODING LEAD

Element	Doe Run Lead, ppm	Corroding Lead, ppm
Ag	3-5	Less than 15
As + Sb	Less than 1	Less than 20
Fe	Less than 1	Less than 20
Ni + Co	Less than 1	-
Cu	Less than 1	Less than 15
Zn	Less than 1	Less than 10
Bi	Less than 1	Less than 500
Cd	1-5	-

TABLE 5 - AVERAGE OPERATING DATA FOR ASP BIPOLAR CELL AND ST. JOE MONOPOLAR CONCEPTUAL CELL PRODUCING LEAD

	ASP Bipolar	St. Joe Monopolar
Current, A	10,000	60,000
Voltage, V	3 x 2.8	10.4
Electrolyte temperature, °C	500-550	450
Electrode current density, A/cm^2	1.1	2.3
Electrode spacing, cm	0.95	0.95
Current efficiency, %	95	90
Lead production rate, kg/h	77	227
Energy requirement, kWh/kg Pb	1.1	1.41

3.3.2 Alcoa Smelting Process (Cont'd)

Lead chloride was fed in solid form, the feed rate being controlled by the bath density. In the bath, the lead chloride content was maintained in the range of 15-40% by weight whereas the electrolyte was a mixture of KCl and LiCl in a weight ratio of 1.4/1.0. Alcoa has shown that for lead production, the energy consumption is so low that the addition of high cost lithium to the electrolyte, to increase the conductivity and reduce power consumption, does not enhance the economics. Therefore, it was suggested that either sodium, potassium or calcium chloride could be used for the electrolyte.

Lead collection in the cell was not optimized during the test work. Tapping was carried out by siphon. Liquid metal accumulated on the cathode plates at the cell bottom to a depth of 20 mm. To avoid short circuits, the control of the metal depth was important. $PbCl_2$ feeding and metal discharging were carried out at different points.

Iron and SO_4 contents in the feed were the major concern. Iron reduced the current efficiency drastically. Formation and accumulation of ferric chloride was prevented by bubbling air, and the resulting oxidation improved current efficiency. Iron formed magnetite and some accumulation on the cathode was observed (up to 8 mm per year). When iron was present it was important to keep oxygen or oxides out of the system. It was suggested that the iron content of the feed should be kept below 50 ppm. SO_4 reacted with the carbon of the electrodes, specifically on the anode surface, and carbon was lost in direct stoichiometric ratio to the O_2 content. In relation to this, the temperature control was an important factor. Above 500°C SO_4 was reduced with carbon, and SO_2 and CO_2 gases were formed. Below 500°C, SO_4 accumulated in the bath.

Alcoa scientists were confident that they have shown that the chlorine handling system was environmentally safe and worked well. During the pilot plant test work, personnel exposure was monitored and the results were reported as satisfactory.

The chlorine gas composition was 95% Cl_2 and 5% N_2 (from purge gases). The gas was at 500-550°C. It was cooled, cleaned from particulates (contained about 0.04 g/l), liquefied and recycled.

3.3.2 Alcoa Smelting Process (Cont'd)

It was suggested that a scale up factor of 11 should be used for scaling up from the pilot plant to commercial scale cell. The approximate inside dimensions would be 305 cm deep x 244 cm x 183 cm with six compartments (bipolar-vertical electrodes). It was estimated that each cell would produce about 30,000 t/y lead.

Alcoa scientists stated that with the technical data they had and with some development work, they could build a commercial scale plant. However to do the development work and finalize the design they would like to build another pilot plant. The pilot plant they had used was dismantled. They are willing to participate in the development work for a fee.

Activities of St. Joe Mineral Corporation in Lead Production by Chloride Metallurgy:

St. Joe had worked on chloride leaching and electrolysis of lead sulphide ores for more than a decade, starting in the late sixties. However, due to the change in government policy on environmental regulations, and generally lower metal prices, they had stopped working on the project. They had worked with Alcoa, Minemet, Duval, Hazen and USBM at different stages. They had built a leaching pilot plant and produced $PbCl_2$ crystals which were shipped to Alcoa, Minemet and Duval for electrolysis. St. Joe signed secrecy/ownership agreements with these companies. It has been stated that all these companies prepared reports on their research work and the reports also included conceptual engineering and cost estimates for projected commercial scale plants.

A conceptual design for a commercial scale cell was prepared based on the results obtained from the pilot scale test work carried out by Alcoa. As noted above, the test work was carried out in a bipolar cell; however, the conceptual design was based on a monopolar cell. It has been projected that to produce 200,000 t/y lead, 7 to 8 bipolar or 60 to 70 monopolar cells would be required. The operating parameters of the conceptual design are listed in Table 5.

According to this conceptual design, the cell inside dimensions were 259 cm x 48 cm x 264 cm long and the outside dimensions were 305 cm x 81 cm x 297 cm long. The cell was made of mild steel and the lining was Duro insulating brick and Korundal XD hard brick. Dry lead chloride was fed from the top at a rate of 306 kg/h and lead was tapped from the bottom to be cast directly into moulds. The electrolyte mix was 45% $PbCl_2$, 23% LiCl and 32% KCl.

3.3.2 Alcoa Smelting Process (Cont'd)

The LiCl/KCl consumption was 0.23 kg/day. Anhydrous chlorine gas was produced at a rate of 79 kg/h. The vertically positioned electrodes were made of graphite, with dimensions of 122 cm x 244 cm x 10 cm thick and their submerged surface areas were 107 x 244 cm. There were one cathode and two anodes in a cell. The life of the electrodes was predicted as 3 to 4 years. Busbars were in series and were made of aluminum.

It was commented that the cell design was simple and that fuming of lead chloride was minimal. However, cell productivity was low, and this would necessitate a large number of cells, with multiple chlorine outlets, for a commercial scale operation.

3.3.3 Hazen Research Molten Salt Electrolysis

Hazen Research Inc. has carried out several programs to investigate the molten salt electrolysis of lead chloride. The ones carried out under the sponsorship of the Cyprus Metallurgical Process Corporation (Cymet) and the St. Joe Corporate Research Center are described briefly below.

Hazen-Cymet Design:

The process, which was developed for Cymet, was based on dry chlorination, brine leaching, lead chloride crystallization and fused salt electrolysis. Extensive laboratory work was followed by the construction and operation of a pilot plant (45).

The electrolyte was 90% by weight lead chloride and 10% by weight sodium chloride. Sodium chloride was selected due to its low cost and it was also possible to bleed impurities from the cell to the brine leach and purification sections. This avoided impurity build up in the electrolyte.

Before feeding to the cell, lead chloride was melted in a special feeder. The cell was designed for a maximum capacity of 166.5 kg of lead per day at a current of 2,000 A. The graphite and molten lead cathode surrounded the graphite anode on the sides and bottom.

At the start-up, the cell contained a heel of lead and a charge of the eutectic salt mix. The cell was heated by electrical resistance elements and when a temperature of 460°C was reached, the power to the electrodes was turned on. The cell became self-heating when the current exceeded 1,000 A.

3.3.3 Hazen Research Molten Salt Electrolysis (Cont'd)

The operating conditions for the cell are summarized in Table 6 and a cutaway view of the cell is shown in Figure 3.

After prolonged operation of the cell, a gradual build up of iron in the fused salt electrolyte was observed, and this resulted in a marked fall-off in cell current efficiency to as low as 50%. The current efficiency returned to normal after purging and replacing the $PbCl_2$- NaCl to an iron content of less than 1 g/l. Recycling the contaminated salt to the brine leach was considered.

Lead produced in the cell was over 99.99% pure and better than the corroding lead (ASTM B29-55) specification given in Table 4.

Based on the results of the pilot scale work a conceptual design for a 50,000 A cell with the production capacity of 159 kg/h of lead was prepared. The cross section of the cell and the layout for a commercial scale plant are shown in Figures 4 and 5, respectively.

It was stated that the process minimized problems such as large cell room floor area, chlorine gas blinding, and rechlorination of lead droplets. In the cell, vertical cathode surfaces and the bottom pool of cathodic molten lead were connected electrically. Chlorine gas could escape from the bottom and sides of the anode. The relatively small vertical dimension of the cell and the electrode spacing of 7.6 cm minimized the rechlorination of lead. It was also suggested that the optimum anode current density would be in the range of 0.6 A/cm^2 to 0.9 A/cm^2 rather than the 1.4 A/cm^2 used in the pilot plant.

Hazen Research Inc. (45) stated that the process was shown to be viable through the laboratory and pilot plant scale test work. It was stated that high purity lead could be produced, with a reasonable power consumption, from a wide variety of sulphide concentrates. However, it was also stated that additional work would be required to provide design data for a commercial scale fused salt cell.

Hazen-St. Joe Design:

Hazen Research Inc. has prepared a conceptual design of a monopolar fused salt cell for a 200,000 tonne per year lead operation for the St. Joe Corporate Research Center (46). The cell design was based on the information available in the published literature on lead chloride electrolysis and related technology on electrolysis of magnesium, aluminum and lithium chloride.

TABLE 6 - OPERATING CONDITIONS FOR A 2,000 A CELL, DESIGNED BY HAZEN-CYMET TO PRODUCE LEAD

Ave. Current, A	1,500
Voltage, V	3.8
Cell temperature, °C	500
Anode current density, A/cm^2	1.4
Cathode current density, A/cm^2	0.3
Electrode spacing, cm	7.6
Current efficiency, %	85
Energy requirement, kWh/kg Pb	1.21
Lead production rate, kg/h	5.2
Anode submerged depth, cm	14.2

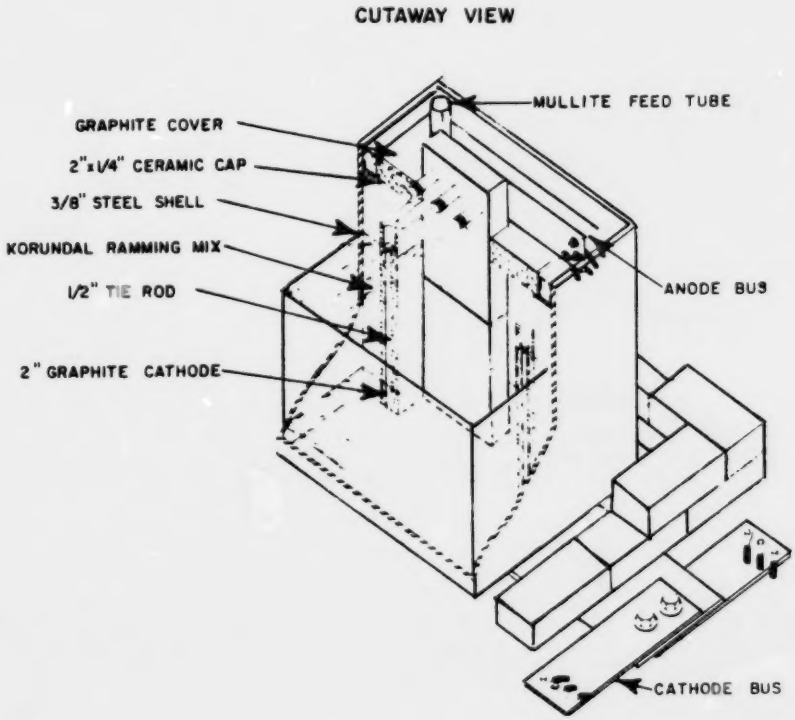
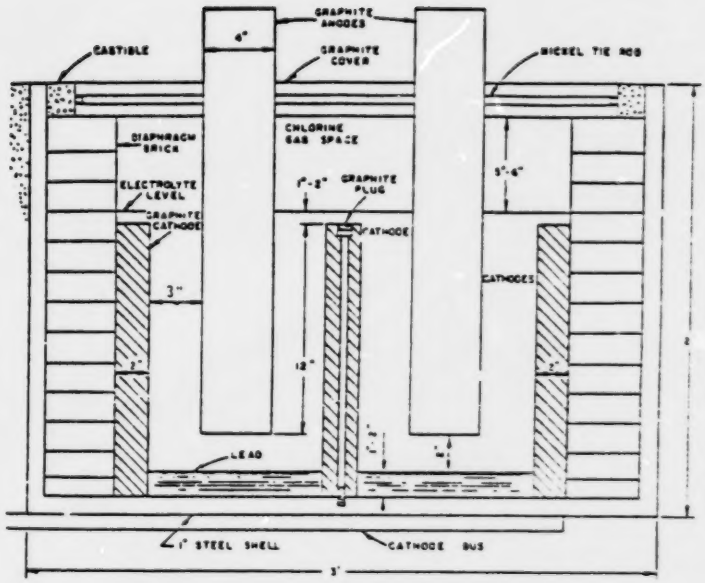


FIGURE 3 A 2,000 A FUSED SALT CELL DESIGNED BY HAZEN RESEARCH INC. FOR CYMET TO PRODUCE LEAD



Active anode area/inch of cell length 56 in^2/inch
Active cathode area/inch of cell length 76 in^2/inch

Anode CD	Anode Length Along Top of Cell	Number of Anodes Per Cell	Total Wt, lb
6 asi	12"	24	2000
12 asi	6"	12	850
18 asi	4"	8	570

Anodes, AGLX, 24" L x 4" x 12"

Cross Section of 50,000 amp Fused-Salt Lead Cell

FIGURE 4 A 50,000 A FUSED SALT CELL DESIGNED BY HAZEN RESEARCH INC., FOR CYMET TO PRODUCE LEAD

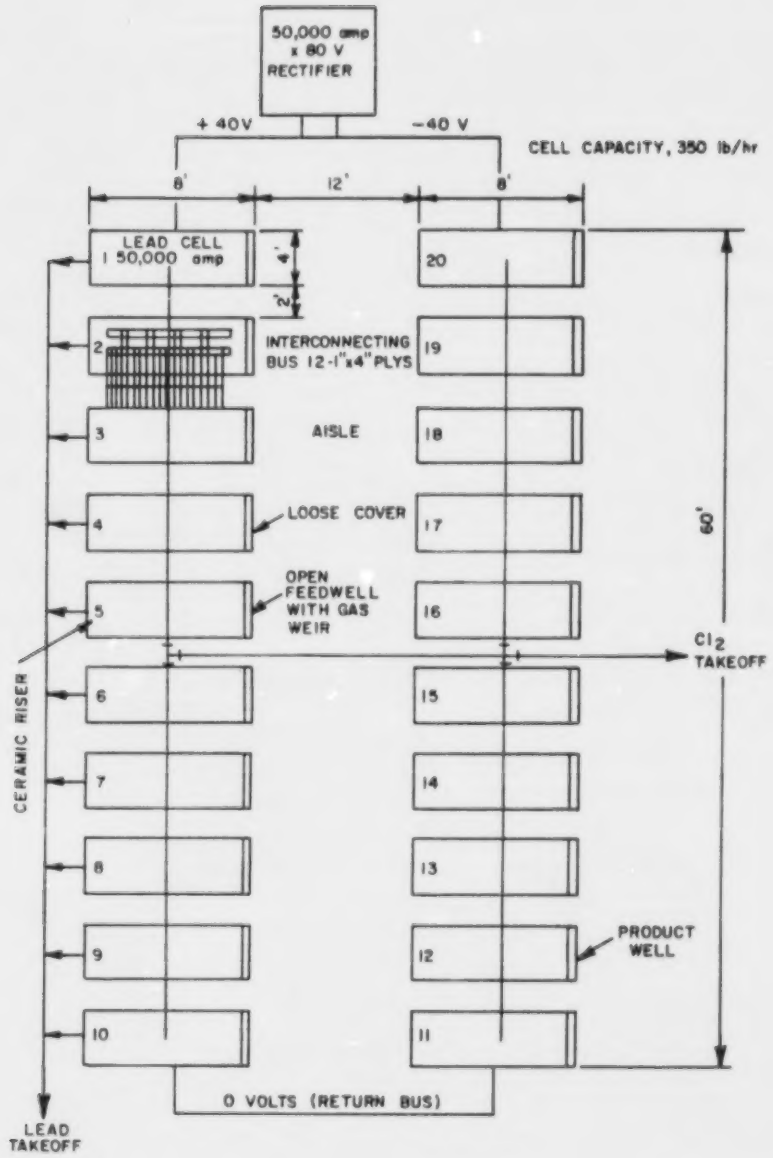


FIGURE 5 A COMMERCIAL SCALE FUSED SALT CELL-ROOM LAYOUT DESIGNED BY HAZEN RESEARCH INC., FOR CYMET TO PRODUCE 24,000 TONNES/YEAR LEAD

3.3.3 Hazen Research Molten Salt Electrolysis (Cont'd)

As a result of extensive optimization studies on various cell design and operating parameters, a cell design was selected and capital and operating cost estimates were prepared (46). Lead chloride was to be fed to the cell as a dry crystalline feed by screw conveyors. A lead product was to be tapped from the cell intermittently, about once per shift. The electrolyte selected was 92% $PbCl_2$ and 8% NaCl.

The operating parameters for the optimum cell design selected by the Hazen Research are listed in Table 7.

It was stated that the monopolar configuration was chosen over bipolar because of the design difficulties associated with devising methods to feed a stack of bipolar electrodes without loss of current via shunt losses. Based on the results of a horizontal bipolar cell operated by the Bureau of Mines (12) that contained two bipolar elements with a current efficiency of 86%, Hazen Research predicted that in order to take full advantage of bipolar design features, the stack would contain up to 10 to 20 bipolar electrodes. This would result in increased shunt losses because of the large potential across the stack and limited heat dissipation due to the narrow electrode gap.

Figure 6 shows the sections of the cell. Electrode faces were inclined about 30° from the vertical. This design was selected for the following reasons:

- Lead deposited on the upward facing cathode would flow to the bottom of the cell and chlorine would flow along the downward facing anode within an envelope. This would allow a closer anode-cathode spacing with a lesser tendency toward back reaction or rechlorination of lead. The main advantage of the proposed design was the operation at high current density and reduced electrode spacing with minimum effect on current efficiency.

- It was stated that horizontal surfaces would require a large floor area and gaseous products from the anode would tend to blind and polarize the anode surface, whereas the vertical surfaces would cause rechlorination of lead. Inclined surfaces would take advantage of the best features of both horizontal and vertical cell designs.

- A cell heat balance had indicated the need for accurate adjustment of the interelectrode gap to stay within the allowable temperature range. The inclined electrode design would permit periodic adjustment of the spacing to allow for electrode wear by erosion and oxidation.

TABLE 7 - OPERATING CONDITIONS FOR A 32,300 A CELL PRODUCING LEAD, DESIGNED BY HAZEN RESEARCH INC. FOR ST. JOE MINERALS CORP.

Current, A	32,300
Voltage, V	3.5
Cell temperature, °C	500
Current density, A/cm^2	0.6
Electrode spacing, cm	2.54
Current efficiency, %	90
Energy requirement, kWh/kg Pb	1.1
Lead production rate, kg/h	112.1

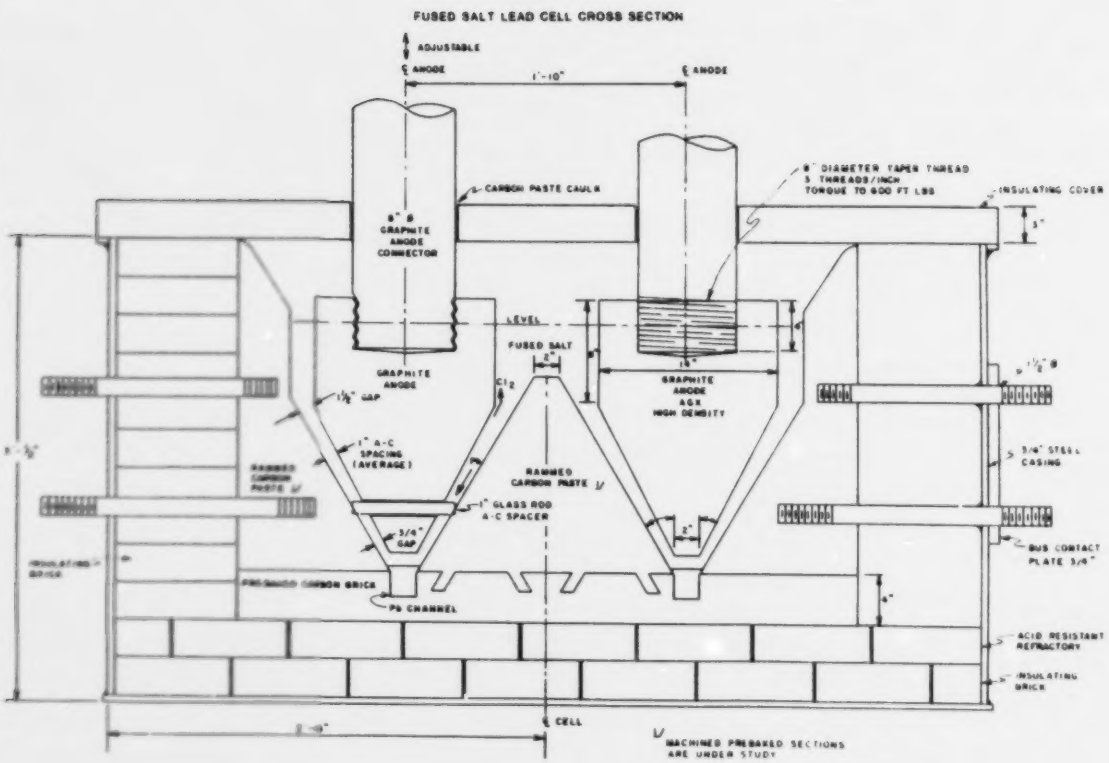


FIGURE 6 - A CONCEPTUAL DESIGN FOR A FUSED SALT CELL PREPARED BY THE HAZEN RESEARCH INC. FOR ST. JOE MINERALS CORP. TO PRODUCE LEAD

3.3.3 Hazen Research Molten Salt Electrolysis (Cont'd)

The anodes were to be made of high density graphite and the cathodes were to be made of prebaked extruded shapes or rammed carbon paste.

Hazen Research Inc. had recommended that the conceptual design be tested with a pilot scale cell of at least 20,000 A capacity.

3.3.4 United Oil Products (UOP) Process

The UOP process was a hydrometallurgical process based on concentrate activation, low temperature chlorination, brine leach, crystallization, drying of lead chloride crystals and fused salt electrolysis (47 and 48). High purity lead was produced in a laboratory scale fused salt cell with an electrolyte of 92% $PbCl_2$ and 8% NaCl. Graphite electrodes were used.

The UOP process was tested only in laboratory scale cells. The fused salt cell was used mainly to complete the flowsheet and show the applicability of electrolysis to the lead chloride produced by the new approach of chlorination. The work was then terminated. The typical operating parameters of the cell are listed in Table 8.

3.3.5 Cominco Hydrometallurgical Process

Cominco developed a hydrometallurgical process to treat complex concentrates containing lead sulphide which comprised the steps of ferric chloride leaching, brine leaching, crystallization of lead chloride and molten salt electrolysis (49). High purity lead containing less than 30 ppm of total impurities was produced in a laboratory scale fused salt cell with an electrolyte of 92% $PbCl_2$ and 8% NaCl.

The fused salt cell was used mainly to complete the flowsheet and show the applicability of electrolysis to the lead chloride produced by the new approach of two-step leaching. The work was then terminated.

Cominco declined to provide any specific information. The typical operating parameters of the cell as listed in their patent (49) are given in Table 9.

TABLE 8 - OPERATING CONDITIONS FOR THE UOP CELL PRODUCING LEAD

Current, A	10
Voltage, V	2.2
Cell temperature, °C	550
Current density, A/cm^2	0.78
Electrode spacing, cm	2.54
Current efficiency, %	97.6
Energy requirement, kWh/kg Pb	0.57

TABLE 9 - OPERATING CONDITIONS FOR THE COMINCO CELL PRODUCING LEAD

Current, A	50
Voltage, V	3.5
Cell temperature, °C	480
Current density, A/cm^2	1.28
Electrode spacing, cm	4
Current efficiency, %	99
Energy requirement, kWh/kg Pb	n.a.
Lead production rate, kg/h	0.2

3.3.6 Alcan-Type Magnesium Cell

Alcan International Limited has developed a process to produce magnesium from magnesium chloride in a fused salt electrolysis cell.

The Alcan-type magnesium cell was developed in Canada in 1940. Based on this process, Aluminum Co. of Canada (Alcan) operated a 10,000 t/y, 30 kA plant in Arvida for some 10 years producing magnesium from brucite ores of the Ottawa region. The operation ceased in 1958. Under a licensing agreement, the plant equipment was sold to Osaka Titanium Co. (O.T.C.) in Amagasaki, Japan. Cells were taken apart, shipped to Japan, and reconstructed. The plant has been in operation since then and Alcan and O.T.C. jointly have been developing the process further. Subsequently, more developed versions of the Alcan-type cell have also been licensed to Oregon Metallurgical Corporation (ORMET) in Albany, Oregon in 1968 and to Titanium Metals Corporation (TIMET) in Henderson, Nevada in 1983. All these plants used the Alcan-type cell as part of their titanium production operations with the Kroll process. The main features of the design and the improvements which were incorporated are described in references 50 through 54.

The process was developed specifically to produce magnesium and successful performance of the cell at 26, 30, 40, 80 and 85 kA has been demonstrated in commercial operations. It was the intent of Alcan to operate the cell at 120 kA (50). The cell in the TIMET plant produces 325 t/y magnesium. There are 48 cells with a total production capacity of 16,000 t/y magnesium.

The main differences between the Alcan-type magnesium cell and the fused salt cell technologies reviewed so far is that the molten magnesium product floats on top of the lectrolyte due to its low density. The electrolyte is a mixture of $MgCl_2$ (18-23%), $CaCl_2$ (20-25%), NaCl (55-58%) and MgF_2 (2%). In each cell there are five high density graphite anodes and five mild steel cathode casings enclosing the anodes. The cell shell is made of reinforced mild steel and the lining is alumina refractory brick. The inside cell dimensions are approximately 280 x 370 x 290 cm deep. The anode dimensions are 120 x 20 x 224 cm high. The width is 20 cm at the top and 8 cm at the bottom. The cell life is almost 3 years. Each cell is provided with AC heating and air cooling devices.

3.3.6 Alcan-Type Magnesium Cell (Cont'd)

Chlorine is 96-97% pure, the balance being air in-leakage. Ducting and piping for the gas handling is made of mild steel. The gas temperature is in the range of 500-600°C. It is cooled, particulates are removed in bag houses containing teflon bags, and it is directed to titanium chlorination.

Typical operating parameters for cells with different capacities are listed in Table 10.

The applicability of this well proven technology to the production of lead is yet to be demonstrated.

3.4 Technologies for Aqueous Electrolysis

3.4.1 Minemet Recherche Process

Minemet has been working since the early seventies on the development of a chloride media hydrometallurgical process to produce lead from sulphide concentrates. The process was based on two-stage ferric chloride or cupric chloride leaching, two-stage purification, aqueous electrolysis. The work has been carried out with laboratory and small pilot scale equipment resulting in development of two flowsheets specifically for electrolysis:

- the first one was a direct electrolysis of leach liquors and produced pure lead while simultaneously reoxidizing the leaching reagent, (ferric chloride) (Figure 8), and

- the second one obtained pure lead from pure lead chloride crystals dissolved in a brine, and generated chlorine (Figure 7).

Based on the favourable results of the small pilot scale cell, a prototype electrolysis cell was built and operated for over two years. The dimensions of the electrodes were similar to those predicted for the industrial scale cell. More than six tonnes of lead was produced and the technical feasibility of the technology was shown (55-61). However, the work was terminated in 1985 due to the general base metals market condition. It was concluded that the technology was developed to the state that the next step would have been to build a commercial scale plant, when and if the lead market would allow.

TABLE 10 - OPERATING CONDITIONS FOR THE ALCAN-TYPE CELLS PRODUCING MAGNESIUM METAL

	O.T.C. Commercial	O.T.C. Prototype	TIMET Commercial
Current, A	40,000	80,000	85,000
Voltage, V	7.3	5.7	6
Cell temperature, °C	660-685	660-675	680
Current density, A/cm^2	1.2	0.8	0.8
Electrode spacing, cm	7.6	5.1	5.0
Current efficiency, %	90	93.2	90
Energy requirement, kWh/kg Mg	18.0	13.9	14.0

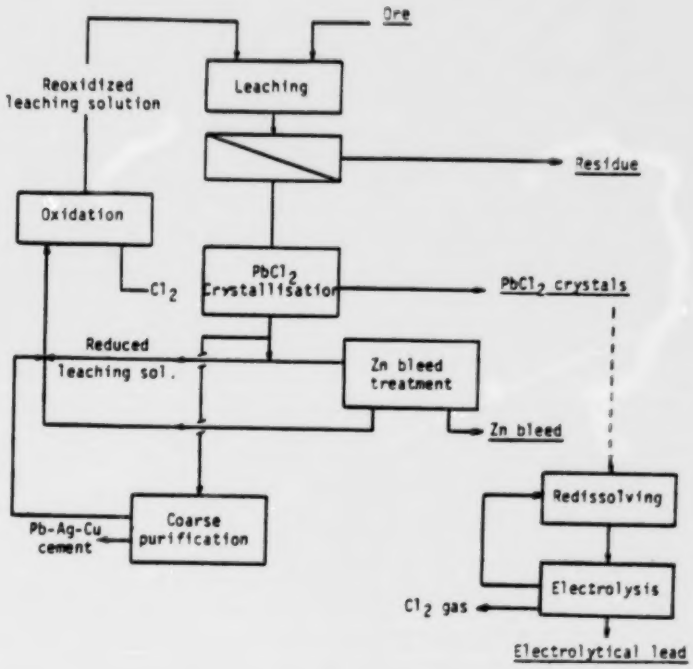


FIGURE 7 - AQUEOUS ELECTROLYSIS PROCESS WITH CHLORINE RELEASE DEVELOPED BY MINEMET RECHERCHE

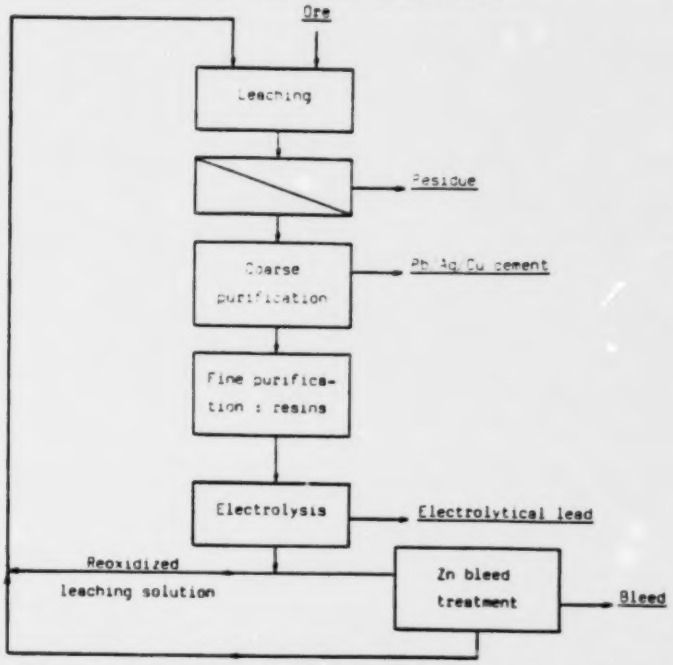


FIGURE 8 - AQUEOUS ELECTROLYSIS PROCESS WITH REOXIDATION OF FERROUS INTO FERRIC CHLORIDE DEVELOPED BY MINEMET RECHERCHE

3.4.1 Minemet Recherche Process (Cont'd)

The first flowsheet, based on electrolysis with reoxidation of ferrous to ferric chloride, worked better with concentrates containing high levels of lead. The second flowsheet was based on the production of lead chloride crystals, subsequently dissolving them in brine, and production of lead and chlorine gas during electrolysis. The second flowsheet was defined as the better for complex ores and eliminated the impurity problem in the product lead. Recent pilot plant work was based on the second flowsheet.

Most of the earlier development work was carried out with the smaller 60 cm x 60 cm cell with one cathode and one anode box. It produced 1 kg/h lead. This cell was operated for as long as 1700 hours without any problem and without removing the cathode from the cell.

The recent work was carried out with the prototype cell which had the dimensions of 300 x 60 x 440 cm long. The cell was made of stratified glass/resin reinforced with a steel frame. Cathodes were made of titanium (Grade 2) and had the dimensions of 150 x 3.5 x 60 cm long. Anodes were made of DSA and had the dimensions of 150 x 4 x 60 cm long. There were 4 anodes and 6 cathodes in 2 packs. The cell produced 15 to 30 kg/h of lead depending on the current density. The cell design is shown in Figure 9.

In the Minemet pilot plant, lead chloride crystals produced by St. Joe also were tested. These crystals were produced by flash crystallization in a vacuum evaporator. Minemet produced lead chloride crystals in a stirred reactor with water cooling coils, in effect a slow cooling process. This produced coarser crystals, up to 200 microns in size rather than up to 138 microns. To filter the crystals, a batch operated vacuum pan filter was used. A continuous belt filter would be preferred in the next design. The moist cake was then transferred to the electrolysis section where it was dissolved in brine.

The solution which had the composition of 250 g/l NaCl (4.3 Mole), 20 g/l Pb^{2+} was fed to the cathode section of the cell. A cation exchange resin was developed to remove impurities such as copper, silver and bismuth from the brine. The resin functions at 80°C under reducing conditions and it was patented under the name of IMACTI GT 73 (100). A second resin with the designation OC 1040 was also developed and a patent application was filed. However, IMACTI GT 73 was preferred since it was possible to strip the impurities and use it again. OC 1040 was more effective in removing nickel and antimony from the brine.

3.4.1 Minemet Recherche Process (Cont'd)

The following were listed as methods of impurity removal from the lead chloride solution prior to crystallization:

- for low copper content; ion exchange resin under oxidizing conditions with air or oxygen is used.
- for zinc and copper together; similarly, ion exchange resin is used with less selective extraction properties.

A comparative study also was carried out between the two types of electrolytes, NaCl + $PbCl_2$ versus NaCl + $FeCl_2$ + $PbCl_2$, in bench scale tests. The first one was determined to be the better.

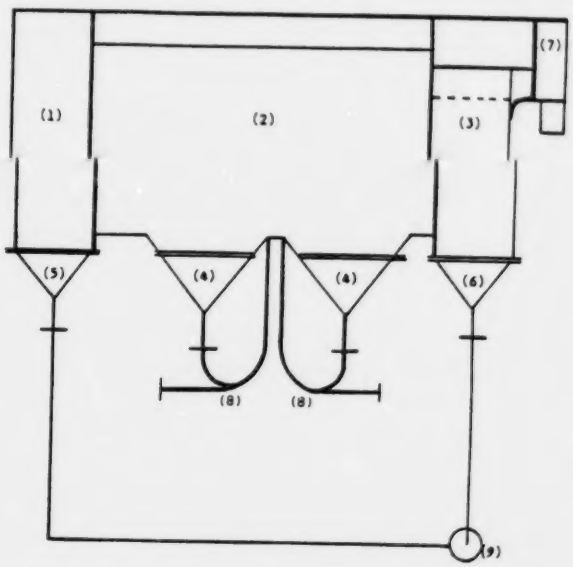
The lead chloride solution was pumped to the cathode compartment, parallel to the cathode surface, at an approximate speed of 10 cm/s through nozzles at the side of the cell. This somewhat high speed was to enhance mass transfer in the vicinity of the cathode and to remove lead crystals from the cathode surface. The solution circulation was 150 m^3/h with a residence time of 1 minute in the cell. After the cell, the solution was collected in a reservoir, the lead chloride level was adjusted, and it was recycled to the cell. The typical operating conditions of the cell are listed in Table 11.

It was commented that a forced circulation of electrolyte was necessary to increase the mass transfer in the anodic compartment where the reoxidation of ferrous to ferric chloride occurs. Having several packages of anodes and cathodes in the same cell in the form of a channel enabled the electrical connections to be non-isopotential for electrodes of the same type, and in the prototype cell having two packs of electrodes enabled the importance of current leaks due to the non-isopotential connection to be determined.

Pure lead crystals were formed in the cathode compartment. They formed sponge-like agglomerates which were pushed, by the forced circulation of the electrolyte, out of the cell through a siphon/hydraulic ejector which had the shape of a goose-neck. The bottom of the cell was of conical shape. Lead agglomerates had a density of about 2 g/cm^3 and could easily be transported in suspension. At the goose-neck, agglomerates compacted together and their density increased to 4-5 g/cm^3 causing settling at the bottom of the goose-neck. Therefore, every 10 minutes the ejector-pump pushed the solution, for a duration of 30 seconds, together with the agglomerates onto a static screen and a double roller compactor (Figure 9).

TABLE 11 - OPERATING CONDITIONS FOR THE MINEMET CELL PRODUCING LEAD

Current, A	4,700
Voltage, V	3
Cell temperature, °C	80
Current density, A/cm^2	0.13
Electrode spacing, cm	5
Current efficiency, %	97.7
Energy requirement, kWh/kg Pb	0.92
Lead production rate, kg/h	15



(1) Feed box (2) Cell body (3) Discharge box (4) Hopper
(5) Divergent (6) Convergent (7) Anodic compartment discharge
(8) Syphon and hydraulic ejector (9) Catholyte accelerator

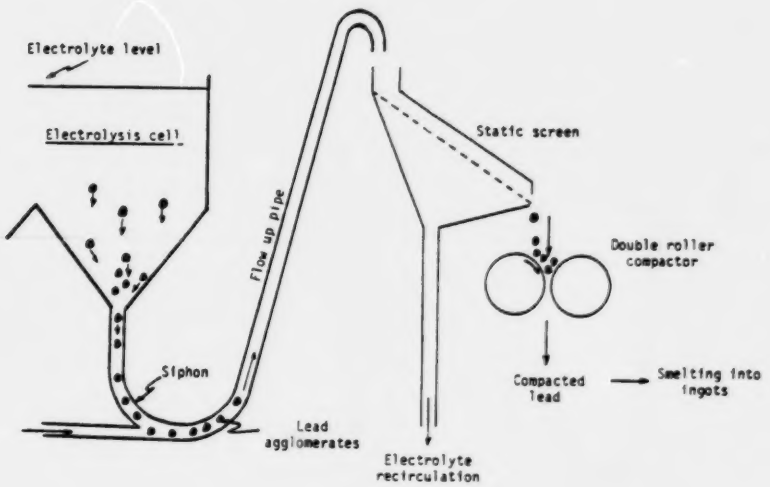


FIGURE 9 - PROTOTYPE CELL DESIGN WITH THE LEAD POWDER REMOVAL AND TREATMENT SYSTEM DESIGNED BY MINEMET

3.4.1 Minemet Recherche Process (Cont'd)

At the screen/filter the solution was separated and recycled. After compacting, lead was melted with NaOH flux and cast into ingots. During melting, about 3-5% lead was lost to slag. It was suggested that each pack of cathodes should have its own ejector. However, a moving belt design (similar to the design adapted in the Duval cell) to serve several cathodes with one ejector for several cathodes also was favoured. As the particle size of the lead crystals was very small, which provided a large surface area, their oxidation rate was fast once they were out of the solution. However, incorporating the system of continuous removal and treatment of lead into the design avoided the oxidation problem (55).

Chlorine ions flowed through the diaphragm and the chlorine gas was released in the anodic compartment. The gas temperature was 80°C. The gas could be compressed or directly recycled back to reoxidation of the leach liquor before the leaching step. For the gas handling, PVC ducting was used.

The anolyte and catholyte compositions were the same and the electrolyte had a variable mean velocity in both compartments.

The cathode-anode arrangement and the current flow were somewhat complicated. The arrangement was to minimize the high current flow in the bus bar. The current flow was in a series pattern which required about 60 cm cathode to cathode distance in the same row. It was commented that this arrangement would result in a larger cell size which would increase the capital cost. The cell voltage was in the range of 3 to 4 V, of this about 2.2 V was the ohmic resistance drop in the solution.

The quality of lead produced was dependent on the electrolyte and it was important not to accumulate high levels of impurities in the leach solution. The lead produced was of high purity and did not require further refining (Table 12).

Several aspects of the cell design were proprietary. They used a special cathode surface treatment procedure which they called "iteration" to increase the durability of the cathodes. The diaphragm and the anode box design were also proprietary and were developed with a similar approach to the one used in the nickel chloride metallurgy. The anode box provided effective collection of the chlorine gas. In the cathode section, and above the cells, there had not been chlorine leakage problems.

TABLE 12 - TYPICAL ANALYSIS OF $PbCl_2$, ELECTROLYTE AND INGOTS IN THE MINEMET PROCESS

ELEMENTS	$PbCl_2$ CRYSTALS (ppm)	ELECTROLYTE (mg/l)	BRIQUETTES (%)	INGOTS (ppm)
Cd	5	1	-	1
Fe	10	12	-	5
Ni	1	2	-	1
S	200 to 1500	150	-	1
Zn	7	5	-	1
Ag	1	1	-	1
Ca	50 to 500	200	-	5
Cu	1.2	1	-	2.4
Mg	5	60	-	5
Ti	-	less than 1	-	1
Na	10	-	0.09	2.1
Cl	-	-	0.16	20

3.4.1 Minemet Process (Cont'd)

For a commercial scale cell, a current of 10,800 A, current density of 1200 A/m^2, dimensions of 260 cm x 100 cm x 800 cm long, volume of 16 m^3, 7 x 3 cathodes and the production capacity of 2000 tonnes lead per year were suggested.

Minemet research staff stated that they would not pursue any test work in the near future. They were completing an economic evaluation study based on the conceptual design of a plant to produce 25,000 tonnes lead per year. The details of the study were not disclosed. They were interested in the further development of the lead chloride electrolysis and were prepared to get involved or provide more information if their technology were to be favoured.

3.4.2 CLEAR Process

Duval Corporation has developed a hydrometallurgical process to produce copper from sulphide concentrates as an alternative to pyrometallurgical processes. The process was named "CLEAR" which is the acronym of the process steps Copper Leach Electrolysis And Regeneration. The process was developed in the early seventies. A commercial scale plant was built near Tucson, Arizona with a production capacity of 36,000 tonnes copper per year. The process was based on leaching concentrates in a chloride medium containing sodium and potassium chlorides, and electrolysis of the solution to produce metallic copper. After a regeneration/oxidation stage, the solution was recycled to the leaching stage (62-67).

Duval Corporation carried out some test work for St. Joe Minerals Corporation on the applicability of the CLEAR process to the electrolysis of lead chloride, and has submitted a report to St. Joe. However, agreement could not be reached between St. Joe and Duval managements on the release of the report to SNC or CANMET. SNC and CANMET were allowed to visit the bench scale test facilities in Tucson, Arizona and meet with one of the senior process engineers.

During the visit to Duval Corporation, discussions were focussed on the process as it was applied to copper production. Some limited comments were made on the test work carried out for St. Joe. Data on dimensions and operating parameters were not disclosed.

3.4.2 CLEAR Process (Cont'd)

Tests were carried out with the cell number 3, which was developed specially for lead production from lead chloride. The cell was of cylindrical shape. The reason for selecting a tubular/cylindrical cell was to reduce the voltage. Lead chloride crystals were provided by St. Joe. The electrolyte was sodium chloride and lead chloride, containing four molar sodium chloride and was roughly equivalent to 10% Na as NaCl and 3% Pb as $PbCl_2$, the balance being water.

The cell was considered to be a bench scale unit, was constructed of FRP and a total of only 20-40 kg lead was produced. Tests were run for only 2-3 days. The copper and iron contents of the lead chloride were critical since they contaminated the lead product.

The cathode was made of copper rod covered with a rubberized material which was bonded to the surface. In the cover, there were deliberate spots to expose copper to provide high current density sites for lead metal deposition. The rod shape provided a more compact cell design and had a larger surface area. There was one cathode in the cell. There was a mechanism to move the rod up and down to shake off any accumulated lead particles. Different sizes of cathodes were tested with lengths of 120 to 180 cm. Cathodes in the shape of plates were also tried. It was commented that plate shape cathodes were preferred since they were known technology and could be vibrated rather than being moved up and down.

There were five or six anodes surrounding the cathode and they had the same diameter as the cathode. Anodes were made of graphite and were placed inside a diaphragm box. Over the anodes there was a removable FRP cover to collect the evolving chlorine gas. The FRP cover was attached to the diaphragm frame/box which limited the escape of gas. The chlorine gas was compressed and dissolved in NaOH. The anolyte solution was continuously recycled to remove the chlorine. A tightly woven membrane was used to separate the catholyte from the chlorine bearing anolyte. The use of such a membrane, together with the slight hydrostatic head in the cathode compartment and the FRP cover prevented any chlorine escape into the open cathode area.

Coarse-grained lead crystals were formed on the cathode. They fell to the bottom by the force of vibration or by gravity. At the bottom, they were collected on a rubber belt conveyor which carried the crystals through a lower density solution floating on the electrolyte and discharged them to a wash pan. After washing, the lead crystals were ready to be melted.

3.4.2 CLEAR Process (Cont'd)

An interesting feature of the cell design was the continuous discharge of coarse-grained lead product by means of a belt-conveyor. This mechanism could be compared with the siphon/hydraulic ejector used in the Minemet cell design.

The CLEAR process has been proven on a commercial scale for producing copper (63). A modified version of it was tried for zinc production (64). Its applicability to lead production however, remains to be proven at a pilot scale.

3.4.3 Cymet Process

Cyprus Mines Corporation together with Hazen Research Inc. and P.R. Kruesi developed a hydrometallurgical process, called the Cymet Process, in the early seventies. The process was based on ferric chloride leaching of base metal concentrates and two stage electrolysis (68-70). The application of the process to chalcopyrite concentrates was shown first in a pilot plant treating 550 kg of concentrate per day. Then a commercial plant was built to treat 23 tonnes of concentrate per day (69).

The applicability of the process to lead sulphide concentrate was demonstrated in laboratory test work and was patented (68). After purification, the solution containing 25 g/l $PbCl_2$ and 3 molar ferrous chloride was continuously fed to the cathode compartment of the cell at a rate of 500 millilitres per hour.

The cathode was made of thin lead sheet and the anode was made of graphite. The cathode and anode compartments were separated by a porous diaphragm of woven polypropylene cloth. The cross section of the diaphragm was 113 cm^2 permitting the solution to flow through the diaphragm at a rate of 4.5 $ml/cm^2/h$. The cathode current density was 0.03 A/cm^2 and the cell current was 2.5 A. Lead was deposited at a rate of 7 g/h at the cathode.

The applicability of the process has to be proven by pilot scale test work.

3.4.4 USBM-Hazen Conceptual Design

The Reno Research Center of the USBM carried out laboratory scale test work on aqueous electrolysis of lead chloride in the early nineteen seventies. The process was based on electrolysis of solid lead chloride in a chloride-base electrolyte on a plate shape lead cathode which was placed at the bottom of the cell. The anode was made of graphite. It was a batch process (13).

3.4.4 USBM-Hazen Conceptual Design (Cont'd)

During electrolysis, chlorine produced at the anode reacted with ferrous ions to generate ferric ions in the leach solution, thus eliminating the need for chlorine handling equipment. At the same time, the $PbCl_2$ was converted to a metallic powder which was not attached to the cathode and could be raked out of the cell, washed, and melted to obtain high-purity lead. Compared to fused salt electrolysis, this process eliminated the requirement for the crystallizer, centrifuge, absorption tower and chlorine handling equipment.

In the electrolysis of $PbCl_2$ the effects of varying electrolyte composition, temperature, current density and electrode spacing were investigated. Spent leach solutions of $FeCl_2$ - NaCl, HCl, NaCl and NH_4Cl were tested as electrolyte in varying compositions (1 to 20% by weight). For each electrolyte composition, the temperature was varied from 25°C to 75°C, the current density was varied from 0.02 A/cm^2 to 0.81 A/cm^2 and the electrode spacing was varied from 1.3 cm to 10.2 cm.

The optimum operating conditions were obtained with 20% HCl at 25°C, using a current density of only 0.02 A/cm^2 and an electrode spacing of 2.54 cm at which the current efficiency was 96% and the power requirement was 0.51 kWh/kg Pb. The lead product obtained was 99.94% pure which met the grade of corroding metal.

Based on this work, a conceptual design for a commercial scale operation was prepared by J.E. Reynolds & Associates (71) and submitted to Hazen Research. The design capacity was 50,000 tonnes per year of lead. It was predicted that it would require 25 cells. A bipolar configuration with sloped electrode surfaces to separate cathode and anode products to avoid rechlorination was used. Electrodes were made of graphite and the electrolyte contained 5% NaCl.

A slurry of spongy lead particles and unreduced $PbCl_2$ crystals would be discharged from the cell. The slurry would then be pumped to a shaking table to make a gravity separation, followed by recycle of $PbCl_2$ slurry to the cells. The cell would be fed by a 50% slurry, direct from a crystallizer, rather than centrifuging and drying. The operating parameters are listed in Table 13 and a sketch showing the cell design is included in Figure 10.

Mr. J.E. Reynolds commented that aqueous cell electrolysis with membrane and bipolar electrodes has the disadvantage of having low productivity for the power consumption. Also at high voltage

TABLE 13 - OPERATING CONDITIONS FOR A BIPOLAR CELL DESIGNED BY HAZEN RESEARCH INC., PRODUCING LEAD

Cell Current, A	2,400
Tank Current, A	31,200
Cell Voltage, V	3
Tank Voltage, V	40
Cell temperature, °C	60
Current density, A/cm^2	0.16
Electrode spacing, cm	5.1
Current efficiency, %	90
Energy requirement, kWh/kg Pb	0.86
Lead production rate, kg/h	108
Number of cells per tank	13

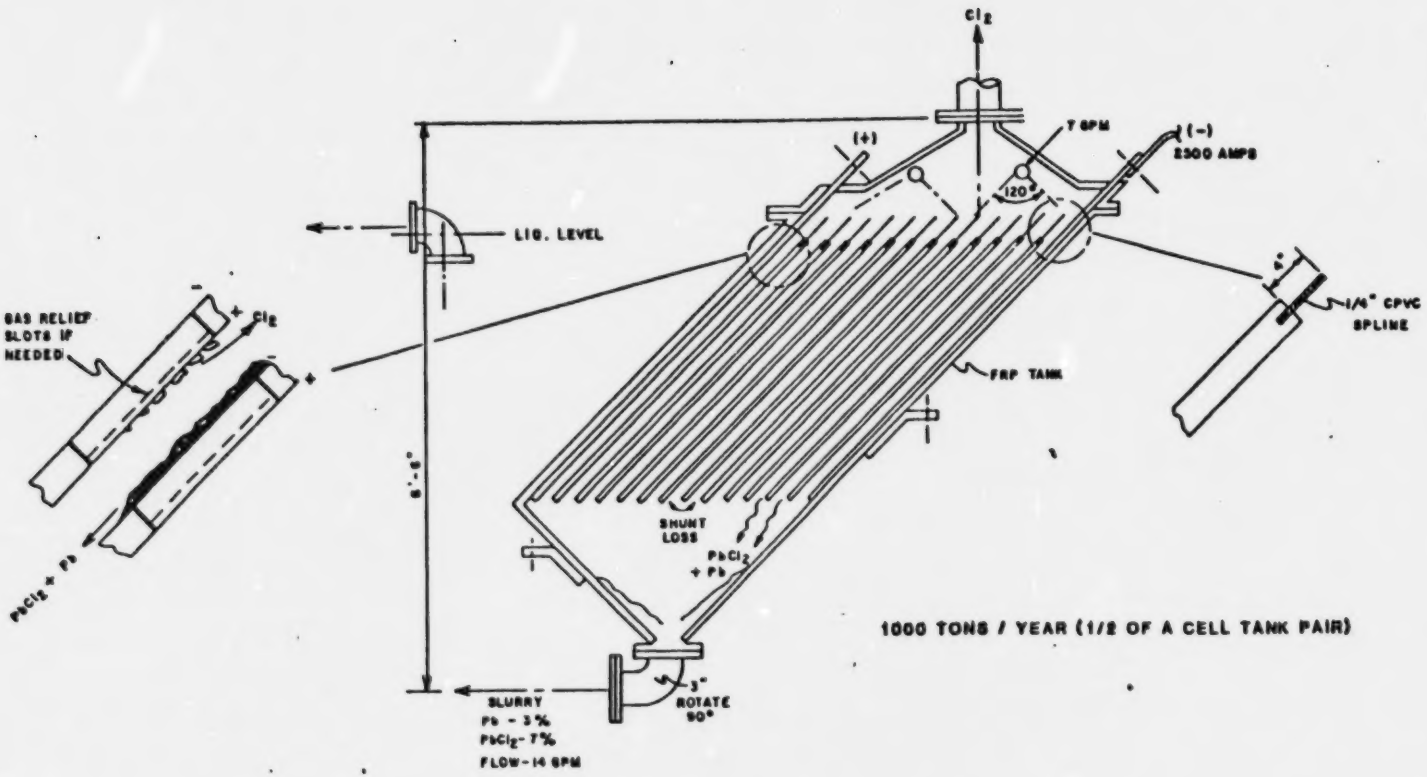


FIGURE 10 - A CONCEPTUAL DESIGN FOR A BIPOLAR CELL PREPARED BY HAZEN RESEARCH INC. TO PRODUCE LEAD

3.4.4 USBM-Hazen Conceptual Design (Cont'd)

and amperage, the electrode surface became sticky. Vibrating the electrodes to remove the accumulation was considered. Titanium electrodes or platinizing the electrodes to provide a smooth surface also were considered. A bipolar cell was preferred to monopolar because it was believed that with the bipolar electrodes a wider range of voltage and amperage could be applied.

3.4.5 Amax Test Work

Amax Research and Development Inc. carried out bench scale test work on the aqueous electrolysis of lead chloride in the early eighties (72).

The lead chloride was produced by ferric chloride leaching of galena concentrate using processes as practised by the USBM and Minemet research centers. The effects of various operating parameters on the nature of the cathodic lead deposits were determined.

In the bench scale cell the anode compartment was completely closed, and the cathode compartment was perforated to allow the free flow of electrolyte. For separating the compartments, a nafion cation exchange membrane or an RAI Research Corporation Anion Exchange Membrane was used. The anode was made of platinized titanium in the shape of a screen. For the cathode, lead foil, copper or stainless steel sheet were tested and lead foil was determined as superior to the others. The cell temperature was varied in the range of 35°C to 60°C.

The electrolysis duration was varied from 2 to 4 hours and the current density ranged from 0.010 A/cm^2 to 0.022 A/cm^2. The typical electrolyte composition was 160 g/l $FeCl_2 \cdot 4H_2O$, 180 g/l NaCl, 20 g/l $PbCl_2$ and 5% HCl by volume. In some experiments, NaCl was replaced by $CaCl_2$ or KCl, and in others, an organic inhibitor (an animal glue identifed as E23) was used.

The cell voltage was varied in the range of 1.3 V to 1.6 V. The current efficiency obtained was in the range of 85 to 96% and the energy requirement was in the range of 0.36 to 0.47 kWh/kg. In the catholyte compartment, a mild agitation by mechanical stirring was provided. In two experiments, nitrogen gas was sparged in front of and below the cathode.

In all of these tests dendrite formation could not be prevented and a totally smooth, compact and coherent lead deposit could not be obtained.

3.4.5 Amax Test Work (Cont'd)

The highest current efficiency was obtained at the operating conditions of 55°C, 0.011 A/cm^2, 1.35 V and with the electrolyte containing NaCl. A combination of 0.4 g/l glue and a low current density of 0.010 A/cm^2 produced the least dendritic of the lead deposits.

The work was terminated after the bench scale testing was completed.

3.4.6 The Research Group of R. Kammel Test Work

The research group of R. Kammel of the Technical University of Berlin, W. Germany developed a ferric chloride leaching and aqueous electrolysis process in the 1970's. The applicability of the process to lead sulphide concentrates was shown with bench scale test work and the process was patented (73-75). The process was based on two stage leaching and two stage electrolysis.

The main features of the cell design were that it did not have a diaphragm or permselective membrane and chlorine was not produced. Two different cell designs were tested.

In the first cell, there were two graphite anodes (74). The cathodes were copper spheres. The spent solution was withdrawn at the anodes and returned to the leaching tank. The cell temperature was 52°C. The current efficiency obtained was 95% and the energy requirement was 0.9 kWh/kg lead.

In the second cell, the cathodes were made of copper plated steel (75) and the anodes were of graphite. The current efficiency obtained was 90% and the energy requirement was 1.05 kWh/kg lead.

The work was terminated after the bench scale testing was completed.

3.4.7 Elkem Test Work

In the 1970's, Elkem A/S, in cooperation with Falconbridge Nikkelverk A/S, developed a ferric chloride leaching process to treat complex sulphide concentrates. The objective was to produce selectively copper, zinc, lead and precious metals (76, 77). From the leaching circuit lead was separated in the form of lead chloride by crystallization. The test work was carried out in pilot plants with capacities of 120 and 1500 kg/day of concentrate. Concentrates were received from various parts of Europe and the technical feasibility of the

3.4.7 Elkem Test Work (Cont'd)

process has been shown. The pilot plant did not include electrolysis of lead chloride crystals. Bench scale test work by molten salt electrolysis was carried out at the Norwegian Institute of Technology (72). However, in this report, the Elkem process has been included under aqueous electrolysis since copper and zinc were electrowon in aqueous electrolysis.

The development work was terminated when Elkem management decided to get out of the copper industry. SNC requested permission to visit the facilities, however, the pilot plant had been dismantled.

3.4.8 Falconbridge Chlorine Leach Process

Falconbridge Nikkelverk A/S of Norway developed a chlorine leach electrowinning process and has been operating a commercial scale plant since 1981 (78). The process is based on leaching converter matte with chlorine whereby nickel and cobalt are dissolved selectively under controlled redox potential and the copper and sulphur remain in the leach residue to be treated further for copper production. The resulting nickel chloride solution is purified from iron, arsenic, lead, cobalt and other impurities by precipitation and solvent extraction. The nickel is then produced by electrolysis.

Electrolysis tank dimensions are 700 cm x 80 cm x 160 cm. Tanks are constructed of reinforced concrete lined with fibre reinforced polyester. In the tankhouse, there are 236 tanks of which 16 are devoted to starting sheet production and the remainder to the production of cathode nickel and Falconbridge crowns. All tanks are equipped with Dimensionally Stable Anodes (DSA). The ones in the crown tanks are spaced 14.5 cm apart and the ones in the cathode tanks are spaced 13 cm apart, accomodating 46 and 53 anodes, respectively.

The anodes are made of titanium coated with an electro-active layer of a noble metal oxides. The anode structure is fitted with a hood to which a diaphragm bag of polyester is attached to isolate the anode. A duct connecting the top of the hood to a manifold running alongside the tank enables withdrawal of chlorine and anolyte by suction.

Electrolyte is fed at one end of the tank and the level is maintained by a small overflow at the other end; the major portion of the electrolyte is withdrawn as anolyte with chlorine. The nickel concentrations in the catholyte and anolyte are 60 g/l and 54 g/l, respectively.

3.4.8 Falconbridge Chlorine Leach Process (Cont'd)

The nickel tankhouse flowsheet and a schematic diagram of the cell are included in Figure 11. The typical operating conditions are listed in Table 14.

The plant management declined the SNC request for permission to visit the plant stating that the company is reluctant to disclose know-how regarding chloride technology.

3.4.9 SLN Nickel Electrolysis Process

The Société Métallurgique Le Nickel (SLN) nickel refinery at Le Havre, France, has been operating a chloride leach-aqueous electrolysis of nickel matte since 1975. The rated capacity of the plant is 16,000 tonnes per year of nickel. The process was developed in the nineteen sixties at MINEMET Recherche, which is the research center for the IMETAL Group (79-80).

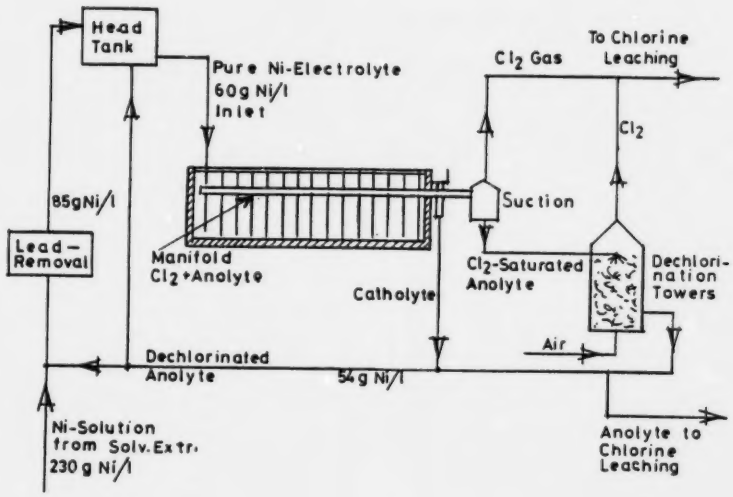
The nickel matte containing 75% nickel and smaller amounts of sulphur, iron and cobalt is crushed and ground before being leached by a ferric chloride solution in the presence of chlorine gas in a reactor-decanter-percolator assembly. The resultant product is a mixture of nickel, cobalt and ferric chlorides. The sulphur remains in its elemental state and is separated from the solution, along with an insoluble residue, in the percolator.

The solution from the leaching is contacted with tri-butyl phosphate, a selective organic solvent, in a battery of countercurrent mixer-settlers. This solvent absorbs the ferric chloride, leaving an iron-free mixture of nickel and cobalt chloride.

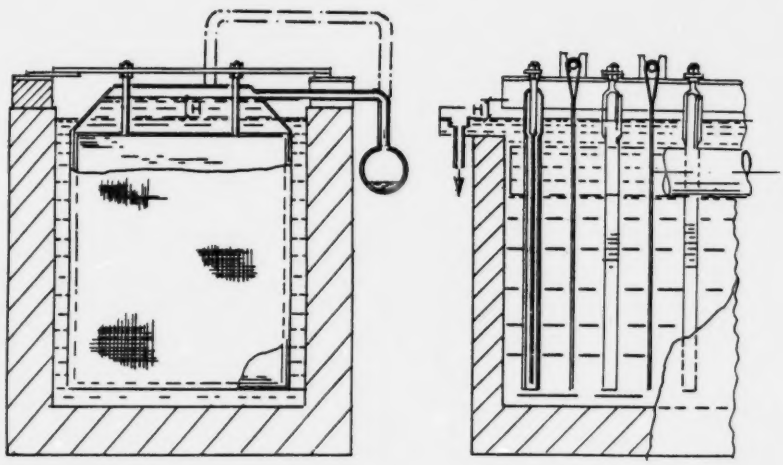
The solvent is recovered by scrubbing with fresh water. Some of the resulting ferric chloride is recycled to the nickel matte leach, and the rest is sold after being concentrated by evaporation.

A similar principle is used to extract the cobalt chloride from the nickel-cobalt chloride solution, using tri-isoctylamine as the solvent.

The nickel chloride solution is then subjected to selective electrolysis, to remove small quantities of lead, and is passed through active carbon to extract any remaining impurities. It is then pumped to the electrolytic tankhouse.



Nickel Tankhouse Flowsheet



Nickel Electrowinning Cell

FIGURE 11 - FALCONBRIDGE NICKEL TANK HOUSE FLOWSHEET AND THE CELL

TABLE 14 - OPERATING CONDITIONS FOR THE FALCONBRIDGE CELL PRODUCING NICKEL

Current, A	24,000
Cell temperature, °C	60
Current density, A/cm^2	220
Electrode spacing, cm	13-14.5
Current efficiency, %	98-99
Inlet flow per tank, m^3/h	4.0
Anolyte flow, m^3/h	3.6
Catholyte overflow, m^3/h	0.4

3.4.9 SLN Nickel Electrolysis Process (Cont'd)

The tankhouse contains 80 electrolysis cells, 15 of which are used to produce nickel cathodes used as starting sheets in the 65 production cells. The starting sheets are produced by deposition on titanium cathodes. Each of the plastic-lined production cells contains 30 cathodes. Anodes are of insoluble graphite. A three- to four-day deposition cycle produces nickel cathodes about 12 mm thick weighing 80 kg.

Chlorine gas produced during electrolysis is recycled for leaching of nickel matte.

The SLN management declined the SNC request for permission to visit the plant stating that the company is reluctant to disclose know-how on the electrolysis technology. However, one may presume that the Minemet lead chloride electrolysis technology (Section 3.4.1) already incorporates the innovative features of this cell design.

3.4.10 Great Central Mines Hydrometallurgical Copper Process

The Great Central Mines (GCM) Hydrometallurgical Copper Process has been developed at the Bacon, Donaldson & Associates Laboratories under a contract with the GCM starting in 1976 (81-83). The applicability of the process to chalcopyrite concentrates to produce high purity copper, silver and sulphur by-products has been shown in a laboratory scale test program. Economic evaluation of the process has been carried out in cooperation with CANMET. A preliminary design and cost estimate for a 6 t/d pilot plant have been prepared. Further work is being carried out to determine the technical and economic viability of the process for application to HBMS copper concentrates.

The process is based on the acidic ferric/cupric chloride leaching of ground concentrate at atmospheric pressure and electrolysis of the chloride solution in diaphragm cells to produce a granular copper product and regenerate a portion of the ferric/cupric chloride lixiviant in the anolyte compartment. Regeneration of the remainder of the lixiviant is carried out with air in a turboaerator, prior to recycling to the oxidation stage of leaching.

Leaching is carried out in two stages with inter-stage thickening to ensure that the pregnant solution being delivered to the electrolysis is in the cuprous/ferrous state. Before the electrolysis, silver is removed by precipitation as an iodide. The leach residue contains gangue, pyrite, sulphur and gold.

3.4.10 Great Central Mines Hydrometallurgical Copper Process (Cont'd)

The electrolysis is carried out in two stages and 87% of the copper entering the circuit is recovered. About 9% of the copper is recycled to leaching and the remaining 4% is recovered in a stripper cell operating at low current density to minimize hydrogen generation. The stripped solution, which is essentially copper free, becomes the bleed stream to prevent iron and impurity build-up in the process.

The cathode is made of stainless steel and the anode is made of graphite. The solution being fed to the cell is comprised of 1 M Cu^{+}, 3.4 M Fe^{2+}, 7.8 M Cl^{-} and 1.5 M HCl while the spent solution is made of 0.08 M Cu^{2+}, 1.9 M Fe^{2+}, 0.8 M Fe^{3+}, 5.8 M Cl^{-} and 3.4 M HCl (82). Typical operating conditions are listed in Table 15.

3.5 Other Related Technologies

3.5.1 Leadex Process

This new process is the result of various testing programs carried out by Tecnicas Reunidas, S.A. of Madrid, Spain. Earlier a process called "The Cuprex Process" was developed to treat complex concentrates (81, 84 and 85). The process was based on ferric chloride leach-solvent extraction-electrowinning for production of copper from complex sulphide concentrates. It has been reported that a pilot plant is being built near Madrid by a joint venture of Nerco Minerals Co. of the U.S.A., Tecnicas Reunidas, and ICI of the U.K. In the solvent extraction stage a patented ICI reagent (DS 543 - a pyridine dicarboxylic acid ester) is used to selectively separate copper from other metals. Then, the copper is produced by aqueous electrolysis.

The Leadex process is based on leaching of lead sulphide concentrate in brine, followed by purification of the leach solution in which silver and impurities are removed by cementation on zinc dust. Lead is recovered from the purified solution by cementation on zinc plates in two stages (Figure 12). The leaching is carried out at a chloride content of 200 g/l and 1.5 to 2.0 g/l iron. The leach operating temperature is 90°C and the pH is maintained at 1.0.

The zinc plates are cathodes produced in the Metclor cell. The liquid effluent from lead cementation, containing zinc, is sent partly to a solvent-extraction system as the aqueous feed solution, where zinc chloride is extracted with a phosphonate, namely di-pentyl pentylphosphonate (DPPP), 50% diluted in kerosene, in two stages. The zinc raffinate is recycled back to

TABLE 15 - OPERATING CONDITIONS FOR THE GCM CELL PRODUCING COPPER

Voltage, V	1.48
Cell temperature, °C	80
Current density, A/cm^2	0.026
Current efficiency, %	96
Energy requirement, kWh/kg copper	0.66
Copper production rate, $g/cm^2/h$	0.06
Copper recovered per pass, %	91
Copper recovered at high current eff., %	87
Copper recovered at low current eff., %	4
Current efficiency in stripper cell, %	63

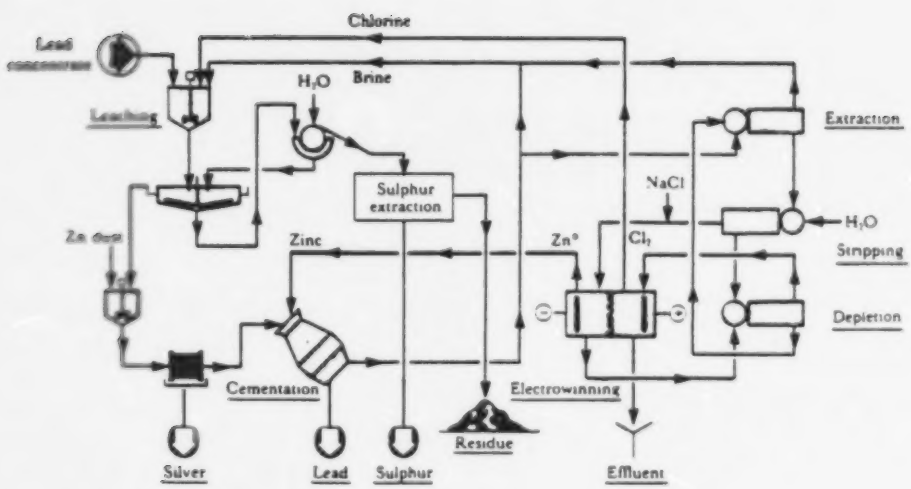


FIGURE 12 THE LEADEX PROCESS FLOWSHEET DEVELOPED BY TECNICAS REUNIDAS S.A. OF SPAIN

3.5.1 Leadex Process (Cont'd)

leaching, and the flowrate is chosen so that a zinc concentration level in the leaching brine is in the range of 40 to 50 g/l.

The zinc organic extract is contacted with hot water in a stripping section consisting of eight stages. The aqueous extract with a zinc concentration of approximately 70 g/l is sent to the Metclor cell as the catholyte after the addition of a given amount of sodium chloride. Zinc is electrowon on titanium cathodes, and a spent catholyte with a zinc concentration of about 25 g/l is produced. The high concentration of chlorides in the spent catholyte allows the extraction of the residual zinc with the organic raffinate from the stripping section in a depletion section comprising four stages.

The aqueous raffinate from this depletion section is an NaCl solution almost free of zinc, which constitutes the anolyte feed to the Metclor cell. Chlorine is evolved in D.S.A. anodes, and sodium is transferred to the catholyte to replace zinc through the membrane. Cathodic zinc is used for lead cementation, while anodic chlorine is used for lead sulphide leaching in brine.

It was reported that a pilot plant with a capacity equivalent to 1 kg of lead per hour was operated continuously for more than 600 hours. Overall solubilization efficiencies above 99 percent for lead and around 94 percent for silver were obtained. Silver cement had a silver concentration between 0.5 and 1.0 percent and could be sold to a precious-metal refinery, or processed further to recover silver, if required. Lead ingots were of commercial grade - 99.97 percent. Elemental sulphur was recovered from the leaching residue by flotation and was further purified by extraction with perchloroethylene and crystallization (85).

It was stated that the Metclor electrowinning cell could be used in principle with any metal chloride solution, providing that a suitable selective extractant was available to achieve the required degree of solution purity to feed the cell. In the cell, a cation selective ion-exchange membrane was used which was called Nafion, developed by Dupont. A schematic of the cell design is shown in Figure 13.

Aluminum, titanium, or the liquid metal itself were tested as the cathode material. D.S.A. anodes, made of titanium activated by ruthenium oxide were used in the cell. Nafion membranes 120, 117 and 114 have also been tested. A slight vacuum (10 mm of water) was applied to the chlorine circuit, allowing safe chlorine handling with minimum risk of leakage to the operating atmosphere. The membrane was pressed against the anode structure

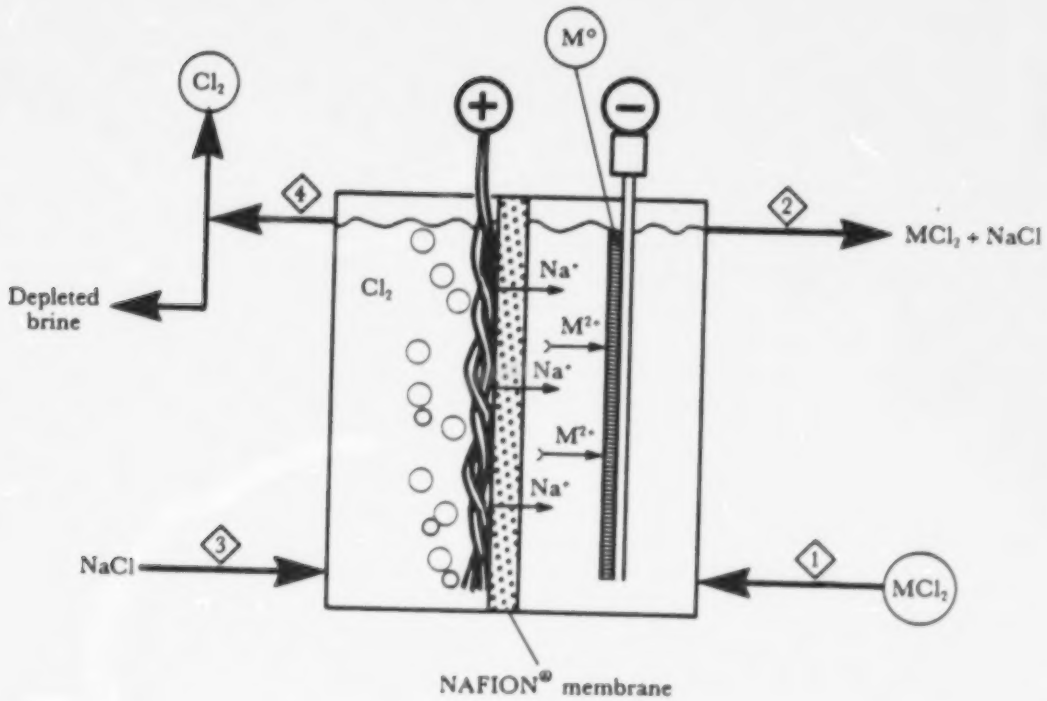


FIGURE 13 THE METCLOR CELL DESIGNED BY TECNICAS REUNIDAS S.A. OF SPAIN TO PRODUCE ZINC OR COPPER

3.5.1 Leadex Process (Cont'd)

by the higher catholyte pressure. The ohmic resistance of the anolyte gap was thus practically suppressed.

It was stated that to make the Metclor cell operate in practice, it was necessary to combine it with a suitable solvent-extraction system, or other technique, able to perform an effective separation of the metal chloride from sodium chloride. They could identify only a few new extractants fulfilling this requirement so that the application of the cell has been limited so far to zinc and copper.

Zinc was produced at a rate of 8 kg/day with an energy consumption of 2.33 kWh/kg zinc. The cell voltage was 2.6 V, the current density was 400 A/m^2 and the operating temperature was 35°C. The cathodic and anodic current efficiences were 94-96% and 92-94%, respectively.

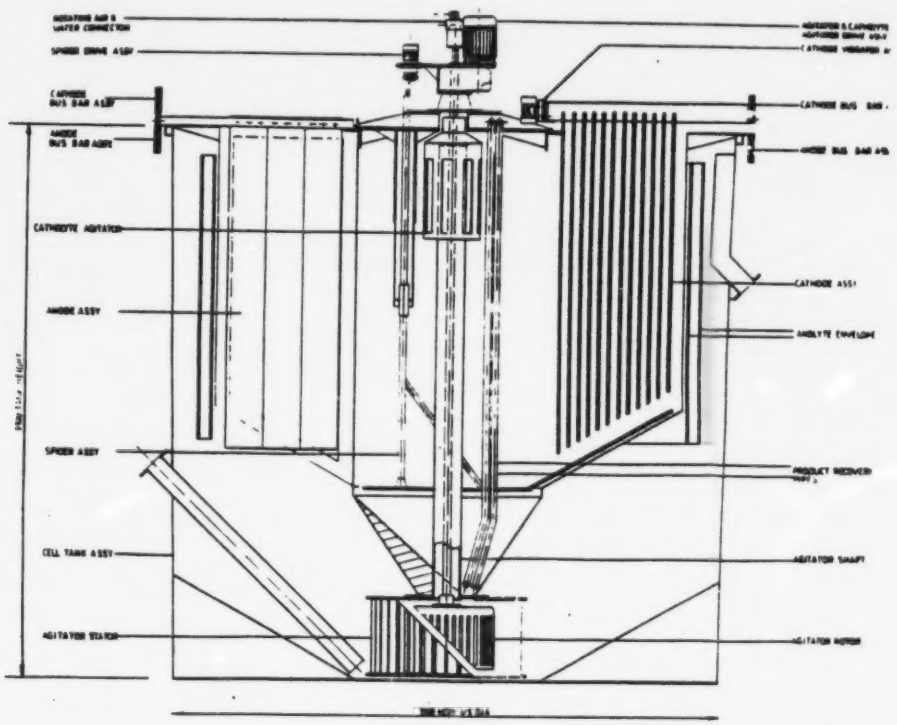
3.5.2 Boliden-Dextec Electrowinning Cell

In the 1970's, Dextec Metallurgical Pty Ltd. of Sydney, Australia developed an electrolytic hydrometallurgical process to treat complex sulphide concentrates for selectively producing lead, zinc, copper and silver. Laboratory scale and pilot scale test work were carried out at the Dextec facilities. Then, under licencing agreements, pilot plant scale test work was carried out by Anglo American Corporation of South Africa to produce copper and by Boliden Metal of Sweden to produce lead (86-90).

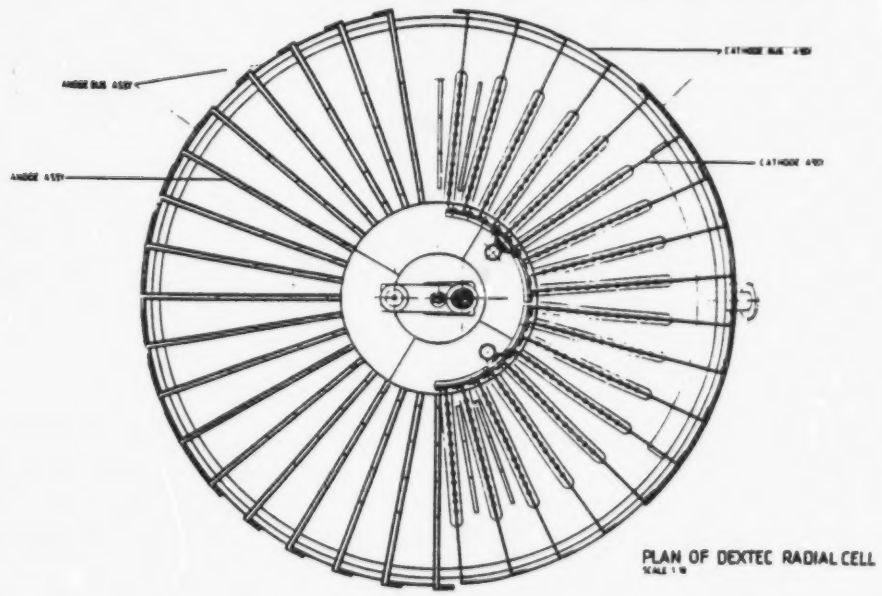
The Dextec lead process itself, and the purpose for which Boliden wanted to use the process, are somewhat different from the CANMET approach. The Dextec lead process treats complex concentrates in a so-called "one-step" and incorporates the ferric chloride leaching and electrolysis into one cell. In other words, with this process leaching and the production of $PbCl_2$ crystals as a separate step are not needed. Boliden used the process to remove lead from copper concentrates and successfully produced lead.

A visit was made to the Boliden Metall facilities by the SNC Study Manager and the CANMET Scientific Authority. A description of the test work or the results obtained had not been prepared by Boliden Metall at the time. The following description of the test work has been written based on the notes made during the visit.

Boliden has built a pilot plant at the mine site at Boliden. The pilot plant was based on a commercial scale cell for which the design drawings were supplied by Dextec. A drawing showing sections of a typical Dextec cell used for copper production is included in Figure 14.



SECTION THROUGH DEXTEC RADIAL CELL



PLAN OF DEXTEC RADIAL CELL

FIGURE 14 - THE DEXTEC RADIAL CELL

3.5.2 Boliden-Dextec Electrowinning Cell (Cont'd)

During the pilot plant work, Boliden modified the cell design and the process to a degree such that they believed they have developed a distinct process which they have called the Boliden-Dextec Electrowinning Cell. The modifications were done with the agreement of Dextec and it was stated that Dextec Metallurgical Pty Ltd. would incorporate these modifications into their design and utilize them in marketing the process in the future. The changes were in the mechanics of the cell, the materials handling system, and the sections where leaching and electrowinning take place. Boliden has made an application to obtain a patent in Sweden on the modified version of the process (91).

The test work was completed in early 1986 and they are not planning to do any more work in the near future. They believe that before building a commercial scale plant the cell and the process need to be modified further. They suggested that a prototype cell should be built before constructing a commercial plant.

Boliden Metall carried out the pilot plant test work over a period of one year. Even though the test results were successful, the Dextec lead process did not solve Boliden's lead problem. Lead enters the smelting circuit from sources other than the concentrate and the high-lead-containing dust still needs to be treated. This would require having two lead recovery plants; one at the mine for concentrate de-leading and one at the smelter to treat the dust. Therefore, the management has decided to stop the test program. However, it was believed that the process would be viable if the concentrates were to be sold in the market, in order to reduce the lead penalty. They were still interested in the process if it were to be further developed by others.

Tests were carried out with two different scale cells, simultaneously. One was the commercial scale cell and the other was a small scale cell. With the small scale cell some development work was carried out to fine tune the operating parameters for the commercial scale cell. In the small cell lead was electrowon at a rate of 0.2 kg/h.

The commercial scale cell was circular in shape with a conical bottom. The inside dimensions of the cell were 3 m diameter, 3 m high and the volume was about 20 m^3. The outside dimensions were 3.2 m diameter and 4 m high. There were 36 radially placed anodes and cathode compartments in the cell.

3.5.2 Boliden-Dextec Electrowinning Cell (Cont'd)

Anodes were made of graphite plates and cathodes were copper tubes with a teflon cover, very similar to the Duval design. The teflon cover was perforated. It was believed that graphite anodes were less expensive and performed better than DSA anodes. The cell shell was made of FRP and had no corrosion problems.

Cathodes were 2 cm in diameter. The length of cathodes varied from 136 cm to 156 cm depending on their location. There were six cathodes per compartment, or 216 cathodes in each cell. Anode plates had the dimensions of 2 cm x 46 cm x 178 cm long.

The original Dextec design had 4 cathode rods for each cathode compartment. Boliden increased this to 6 rods. Each cathode assembly had its own loose diaphragm bag and at the bottom there was a glass fiber spider to discharge the lead crystals. These spiders were mechanically agitated. Problems with the diaphragm bags and the spiders were recorded by Boliden. It was stated that the Minemet design, which was a rigid-plastic frame and diaphragm tightly stretched on the frame, was better. It was also suggested that, similar to the Falconbridge nickel plant in Norway, a polyester fabric diaphragm might have been better than the non-woven polypropylene they used.

The cell was operated as a batch process. It was operated about 10 to 12 hours per day and in two-week campaigns. Various copper concentrates from different locations were treated successfully. The composition of the concentrates varied in the range of 10-25% Cu, 4-20% Pb, 4-30% Zn, 20% Fe, 100-20,000 ppm Ag and 1-20 ppm Au. Galena could be leached selectively in five hours at low ferric chloride concentrations. Lead recovery was greater than 93%.

The formation of ferric ions took place at the upper section of the cell and concentrates settled at the bottom away from the electrodes. For effective leaching, special agitators were designed for mixing and flocculants were added. Boliden also increased the height of the leaching zone in the cell by about one meter.

Concentrates were slurried in a mixing tank with spent electrolyte, and HCl to decompose carbonates. 250 g/l NaCl and zero to ten liter HCl per tonne concentrate (depending on the concentrate) were added. The lead content in the solution was 20 g/l. In the anode compartment, the lead content varied in the range of 20-25 g/l and in the cathode compartment it was 15-20 g/l. The concentrate slurry was fed to the anode

3.5.2 Boliden-Dextec Electrowinning Cell (Cont'd)

compartment where galena was leached with ferric chloride. Ferric (Fe^{+3}) concentration was less than 10 mg/l. Any Fe^{+2} formed was reoxidized at the anode. The pH level was kept in the range of 0.5 to 2.0.

Basic chemical reactions were:

$$PbS + 2FeCl_3 \longrightarrow PbCl_2 + 2FeCl_2 + S^\circ$$

$$PbS + 2HCl \longrightarrow PbCl_2 + H_2S$$

$$H_2S + 2FeCl_3 \longrightarrow 2FeCl_2 + 2HCl + S^\circ$$

Less than 0.1% of the copper and less than 1% of both iron and zinc were dissolved. Copper in the solution was kept at less than 10 mg/l. Any copper leached to the solution ended up in the product lead.

The five hour leaching time was considered relatively slow. Other processes, including conventional ferric chloride leaching, were tried but the same degree of recovery and selectivity could not be achieved. However, only copper concentrates and not bulk concentrates were tested.

The original Dextec process design did not include purification of anolyte before pumping into the cathode compartment. Boliden discovered that purification was necessary to produce high purity lead. Lead or iron powder were used for purification, by cementation at 80-90°C. Lead loss was minimal due to the NaCl concentration of 250 g/l.

Elemental sulphur and unleached concentrate remained at the bottom of the cell. Diaphragm blinding problems were not recorded. Anode-cathode distance was 7 cm. The current efficiency was higher than 95% and the energy requirement was 0.6-0.7 kWh/kg lead. The current density was 350 A/m^2 at the anodes and was higher at the cathodes. About 600-700 kg/h of concentrate could be treated and about 40 kg Pb per hour was produced. The cell operating temperature was 80-90°C. Chlorine or H_2S leakage problems were not recorded. Typical operating conditions are listed in Table 16.

It was believed that the lead discharging system needed to be redesigned and that the number of lead discharge locations should be reduced. Lead crystals were 1 to 2 mm in size and were sucked from the bottom of the cell. The particle size did not cause

TABLE 16 - OPERATING CONDITIONS FOR THE BOLIDEN-DEXTEC ELECTROWINNING CELL PRODUCING LEAD

Current, A	24,000
Voltage, V	2.5-3.0
Cell temperature, °C	80-90
Current density, A/cm^2	0.035
Electrode spacing, anode/cathode, cm	7
Electrode spacing, anode/anode, cm	16
Current efficiency, %	95
Energy requirement, kWh/kg lead	0.6-0.7
Lead production rate, kg/h	40
Concentrate feed rate, kg/h	600-700
Lead recovery, %	93

3.5.2 Boliden-Dextec Electrowinning Cell (Cont'd)

handling problems and they could be melted without high losses. Crystals did not stick and dendrites did not form at the diaphragm. By increasing the lead content in the solution, the particle size could be increased. A crystallizing agent was used. Cathodes were mechanically vibrated every 10 minutes for six seconds. However, most of the time this was not needed since lead crystals fell easily. Lead particles were first collected at the bottom of the cathode compartments and the spiders discharged the lead to a central-common discharge point. Boliden modified the bottom and made it steeper to enhance the lead fall and eliminate the clogging problem experienced earlier.

Lead produced was not high purity. This, however, was not a problem as Boliden has a lead refinery at site. The product lead, without having solution purification in the process flowsheet, had impurities of 0.2% Ag, 0.1% Cu, 0.1% Fe, 0.1% Zn, 0.2% NaCl and sometimes 0.1% Bi.

Lead crystals were filtered on a belt filter and washed with the brine and water to remove lead chloride and other chlorides. Lead sponge was compacted and remelted. Elemental sulphur remained in the concentrate. The slurry after lead removal was discharged from the cell. Operating a full circuit was not tried. 2-3% of the solution was bled to neutralization. At any time there was 20 m^3 solution in the cell containing 5 to 6 tonnes concentrate.

It was estimated by Boliden that a cell producing 50 kg Pb/h (15,000 Amp) would require a capital cost of US $115,000 and without capital charges the operating cost would be US $0.27/kg lead. 60-80 cells would be needed to produce 30,000 tonnes lead per year.

The Dextec process is being marketed to produce copper, zinc and silver as well as lead. In comparison to a rectangular cell the Dextec radial cell occupies less space and accommodates more anodes.

3.5.3 AMT Lead Process (Hazen)

The Advanced Minerals Technology (AMT) Lead Process was based on cupric chloride leaching of lead sulphide concentrates followed by a brine pressure leaching of lead chloride and the unreacted sulphide gangue to separate the elemental sulphur and the gangue to produce relatively pure lead chloride brine. Lead chloride was crystallized and further refined during the crystallization. Lead chloride crystals were then reduced by hydrogen at about 800°C in a specially designed furnace.

3.5.3 AMT Lead Process (Hazen) (Cont'd)

The process was developed by Hazen Research Inc. in the early eighties. A pilot plant was built, but before the test work had started, the investor died and the project was subsequently abandoned (92, 93).

It was commented that among the methods which have been tried at the Hazen Research Inc., this was considered to be superior. Hydrochloric acid, moisture and high temperature did not cause a corrosion problem. Hydrogen reduction is not easy but it is cost effective. In requires only one or two reactors compared with a series of cells. It is also considered to be better from the point of view of working environment.

The process offers an alternative to the electrolysis of lead chloride, but has yet to be proven at a pilot scale operation.

3.5.4 Hazen Carbon Reduction Process

The process was based on the conversion of lead chloride to a compound of $PbCO_3$ and PbO with calcium or sodium carbonate and reduction in a furnace with carbon. It was considered as an alternative to hydrogen reduction in the AMT process. It had the problem that removal of excess calcium or sodium from the circuit necessitated an additional step to the process. Very limited test work had been carried out and there is no publication available.

The process offers an alternative to electrolysis of lead chloride, but its technical feasibility has to be proven.

4.0 RESULTS OF APPRAISAL OF METAL CHLORIDE ELECTROLYSIS TECHNOLOGIES AND COMPARISON BETWEEN FUSED SALT ELECTROLYSIS AND AQUEOUS ELECTROLYSIS

4.0 RESULTS OF APPRAISAL OF METAL CHLORIDE ELECTROLYSIS TECHNOLOGIES AND COMPARISON BETWEEN FUSED SALT ELECTROLYSIS AND AQUEOUS ELECTROLYSIS

4.1 General

A comparison between fused salt electrolysis and aqueous electrolysis has been carried out based on the technical/economic appraisal of the existing emerging metal chloride electrolysis technologies. The objective was to identify the superior lead chloride electrolysis technology, or the superior features of the technologies, in order to initiate a conceptual design of an electrolytic cell which could treat lead chloride crystals or solution produced by the ferric chloride leach process developed by CANMET.

4.2 Results of the Appraisal of the Existing and Emerging Metal Chloride Electrolysis Technologies

The potential of producing lead, and other base metals ,from sulphide concentrates or ores in a chloride medium has been under consideration for several decades. Since the sulphur dioxide emissions from non-ferrous metals smelters became an environmental issue, the interest in trying to develop alternative processes has increased. In recent years, this interest has been enhanced, as the search for technically and economically feasible processes to treat complex base metal ores has intensified.

Results of several evaluation studies on the technologies to treat sulphide concentrates through leaching and electrolysis in a chloride medium have been published (94-98). In these evaluations, commonly stated concerns were the problems related to the corrosion of equipment in contact with chlorine or chloride compounds, the quality of the working environment, and other technical uncertainties since these processes were not proven at a sufficiently large scale of operation.

The present appraisal has shown that with the developments that have taken place in the commercial scale production of aluminum, magnesium, nickel, and copper in chloride media, these concerns are no longer justified.. The applicability of both leaching in a chloride medium and electrolysis, either in a fused salt or aqueous electrolyte, to produce lead from sulphide concentrates have been proven in pilot scale operations. The companies which are involved in developing these technologies state that after a short test program with a prototype unit, they would be able to build commercial scale plants.

4.2 Results of the Appraisal of the Existing and Emerging Metal Chloride Electrolysis Technologies (Cont'd)

It can be stated that, today it is technically feasible to produce lead from lead chloride crystals, or solution, by electrolysis without experiencing major problems with respect to:

- corrosion of the equipment used
- the working environment
- the off-gas handling and cleaning
- the mechanical structure and operation of the electrolytic cell, and
- the quality of the lead produced.

However, the economic competitiveness of lead chloride electrolysis with the existing pyrometallurgical processes has yet to be proven, since there is as yet no commercial scale operation utilizing this technology. One study on this aspect has shown that for less than 10,000 tonnes lead production per year, in a remote region near to the mine or concentrator site, the chloride leach-electrolysis process would be financially attractive (99).

During the visits to the research centers and production facilities, some internal capital cost estimates for both types of electrolysis were mentioned. These estimates had not been published and it was not possible to review and compare them. They indicated that, for an electrolysis plant producing 30,000 tonnes of lead per year, utilizing either fused salt electrolysis complete with chlorine collection and compression or the aqueous electrolysis process, the capital cost requirements would be in the range $6.5 million to $12.0 million, in 1986 dollars.

In the absence of sufficient data it is not possible to carry out an accurate economic evaluation of fused salt electrolysis compared with aqueous electrolysis. An economic comparison would only be indicative, based on the information available concerning operating parameters and the electrolytic cell design, obtained by pilot plant scale operations.

In Table 17, a list of the chloride electrolysis technologies, reviewed in this appraisal together with their stages of development, metal produced and their status is summarized. It is interesting to note that out of 22 technologies reviewed only three of them (Alcan-Type Magnesium Cell, Falconbridge and SLN) are operating at a commercial scale, two of them (GCM and Cuprex) are progressing from the laboratory scale to a pilot scale operation and none of these are on lead production. It should be noted that even though Boliden Metall has terminated the development work with the Dextec lead process, Dextec Metallurgical Pty Ltd. is still marketing the technology actively. However, as noted earlier, this process is not applicable to the ferric chloride leach-electrolysis approach of CANMET.

TABLE 17 - STAGE OF DEVELOPMENT AND STATUS OF CHLORIDE ELECTROLYSIS TECHNOLOGIES REVIEWED

Technology	Stage of Development	Metal Produced	Status
FUSED SALT ELECTROLYSIS:			
USBM	Pilot Plant	Lead	Terminated
ASP	Pilot Plant	Lead	Terminated
St. Joe	Conceptual Design for Commercial Scale	Lead	Terminated
Mazen/Cymet	Pilot Plant	Lead	Terminated
Mazen/St. Joe	Conceptual Design for Commercial Scale	Lead	Terminated
UCP	Laboratory Scale	Lead	Terminated
Comanco	Laboratory Scale	Lead	Terminated
Alcan-Type Mg Cell	Commercial Scale	Magnesium	Operating
AQUEOUS ELECTROLYSIS:			
Minemet	Pilot Plant	Lead	Terminated
CLEAR/Duval	Laboratory Scale	Lead	Terminated
Cymet	Laboratory Scale	Lead	Terminated
USBM/Mazen	Lab. Scale/Conceptual Design for Commercial Scale	Lead	Terminated
Amax	Laboratory Scale	Lead	Terminated
H. Kammel	Laboratory Scale	Lead	Terminated
Elkem	No Cell Design	Lead	Terminated
Falconbridge	Commercial Scale	Nickel	Operating
SLN	Commercial Scale	Nickel	Operating
UCM	Laboratory Scale	Copper	In Progress
OTHER RELATED TECHNOLOGIES:			
Leadex	Pilot Plant	Lead/Zinc	In Progress[1]
Boliden/Dextec	Pilot Plant	Lead	Terminated[2]
ANT	Laboratory Scale	Lead	Terminated
Mazen Carbon Reduction	Limited Test Work	Lead	Terminated

[1] A pilot plant is being built to test the version called "the Cuprex Process" to produce copper.

[2] Boliden Metall terminated the development work. Dextec Metallurgical Pty Ltd. has been actively marketing the technology.

4.2 Results of the Appraisal of the Existing and Emerging Metal Chloride Electrolysis Technologies (Cont'd)

Among the technologies being developed to produce lead, three fused salt electrolysis (USBM, ASP and Hazen/Cymet) and one aqueous electrolysis (Minemet) technologies have been proven in pilot scale operations. For these technologies, the next stage would be to build a prototype commercial scale plant. However, due to the general depressed economic situation in the base metals industry, no one has yet made the necessary investment.

4.3 Comparison of Fused Salt Electrolysis with Aqueous Electrolysis

From the fused salt electrolysis technologies reviewed, five of them have been selected for comparison with the aqueous electrolysis technologies listed in Table 18. Of these five technologies, three of them are pilot plant operations and two of them are conceptual designs for commercial scale operations.

Similarly, from the aqueous electrolysis technologies reviewed, two of them have been selected for the comparison study. Of these two technologies, one of them is a pilot plant operation and the other one is a conceptual design for a commercial scale operation.

The lead chloride electrolysis processing routes and the cell technologies identified as applicable to the leaching process flowsheet of CANMET are summarized in Figure 15. Out of the four routes, direct feeding of either the lead chloride crystals to the fused salt cell or the lead chloride solution to the aqueous electrolysis cell are relatively simpler than redissolving the crystals in a brine solution or melting the crystals prior to feeding to the electrolysis cell.

A design for an aqueous electrolysis based on bipolar electrodes was proposed by the USBM and Hazen Research Inc. However, it was not developed any further. The Minemet Recherche Process utilizes monopolar electrodes.

One of the major differences between the two most advanced fused salt electrolysis processes, the USBM Process and the Alcoa Smelting Process, is the electrodes. The USBM Process is based on monopolar electrodes while the Alcoa Smelting Process is based on bipolar electrodes. The bipolar electrodes are known to provide higher productivity.

Based on the information available, among the processes directly applicable to the ferric chloride leach process developed by CANMET, the USBM Molten Salt Electrolysis Process and the Alcoa Smelting Process have been considered as the most advanced

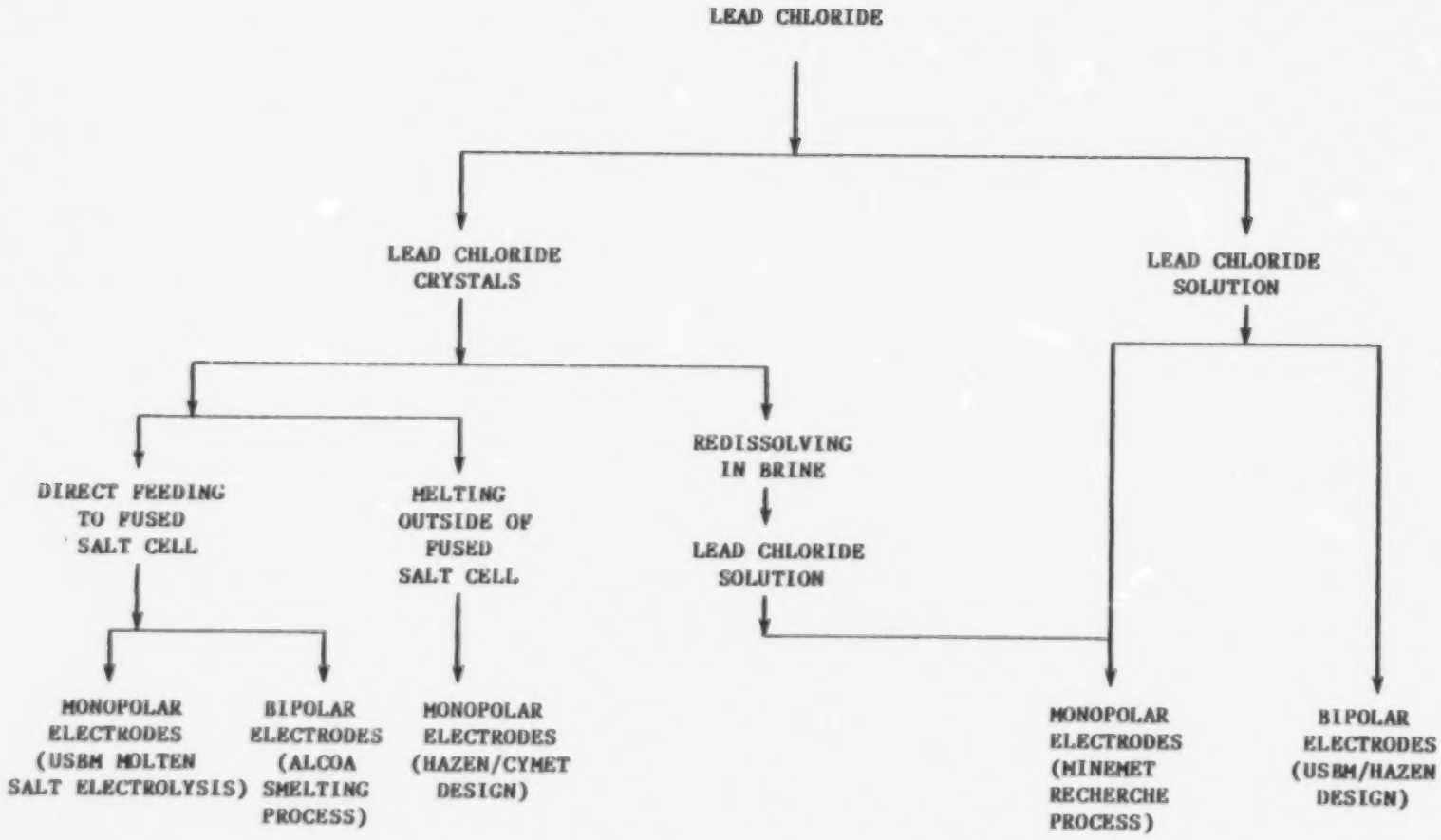

LEAD CHLORIDE
LEAD CHLORIDE CRYSTALS
LEAD CHLORIDE SOLUTION
DIRECT FEEDING TO FUSED SALT CELL
MELTING OUTSIDE OF FUSED SALT CELL
REDISSOLVING IN BRINE
LEAD CHLORIDE SOLUTION
MONOPOLAR ELECTRODES (USBM MOLTEN SALT ELECTROLYSIS)
BIPOLAR ELECTRODES (ALCOA SMELTING PROCESS)
MONOPOLAR ELECTRODES (HAZEN/CYMET DESIGN)
MONOPOLAR ELECTRODES (MINEMET RECHERCHE PROCESS)
BIPOLAR ELECTRODES (USBM/HAZEN DESIGN)

FIGURE 15 OPTIONS FOR LEAD CHLORIDE ELECTROLYSIS

TABLE 18 - TYPICAL OPERATING PARAMETERS FOR SELECTED LEAD CHLORIDE ELECTROLYSIS TECHNOLOGIES

TYPICAL OPERATING PARAMETERS	FUSED SALT ELECTROLYSIS					AQUEOUS ELECTROLYSIS		RELATED TECHNOLOGIES
	USBM[1].	ASP	HAZEN/CYMET	ST. JOE[3].	HAZEN/ST.JOE[3].	MINEMET	USBM/HAZEN[2,3].	BOLIDEN/DEXTEC
Current, A	3,000	10,000	1,500	60,000	32,300	4,700	2,400	24,000
Voltage, V	2.5	8.4	3.8	10.4	3.5	3.0	3.0	2.5-3.0
Cell temperature, °C	450	500-550	500	450	500	80	60	80-90
Current density, A/cm^2	0.36	1.1	1.4	2.3	0.6	0.13	0.16	0.04
Electrode spacing, cm	1.27	0.95	7.6	0.95	2.5	5.0	5.1	7.0
Current efficiency, %	99	95	85	90	90	98	90	95
Production Rate, kg/h	11	77	5	227	112	15	8.4	40
Energy Requirement, kWh/kg	0.66	1.1	1.2	1.4	1.1	0.92	0.86	0.6-0.7

1. Cell with sawtooth electrode.

2. For one cell in a tank containing 13 cells.

3. Conceptual design based on test work.

4.3 Comparison of Fused Salt Electrolysis with Aqueous Electrolysis (Cont'd)

representatives of fused salt electrolysis, while the Minemet Recherche Process has been identified as the most advanced representative of aqueous electrolysis. The inventors of these three technologies stated that they have demonstrated the technical feasibility of producing high quality lead. The key to impurity control in the lead product in all three processes was to produce high purity lead chloride, which is now established as a general requirement for lead chloride electrolysis.

Typical operating parameters for both USBM and Minemet technologies, listed in Table 18, indicate that electrolysis requires about 30% more energy with the Minemet Process compared to the USBM process. In practice, this difference might be even higher since the compacted lead crystals would need to be melted which would require additional energy. This is not the case with the USBM process, since lead is produced in the molten state and can be cast directly.

In the USBM cell design, the energy requirement per unit weight of lead produced was reduced from 1.32 kWh/kg Pb to 0.66 kWh/kg Pb by reducing the anode/cathode distance from 19 mm to 13 mm, by changing the shape of electrodes from the flat plate to the sawtooth, and by facilitating increased removal of chlorine gas from the anode surface.

The reduced electrode spacing resulted in reduced voltage drop, which increased the current efficiency. The sawtooth shape electrodes provided a 50% increase in the electrode surface area, which resulted in a reduction of current density from 0.68 A/cm^2 to 0.36 A/cm^2 (Table 2). The increased removal of chlorine gas from the anode surface was achieved as a result of machining 13 mm holes in the anodes.

The practicality of maintaining this reduced electrode spacing, the optimum shape of the sawtooth graphite electrodes with holes, and the cost of preparation of these electrodes, are aspects which have to be investigated further for larger scale cells.

In Table 19 the configuration, dimensions and types of the cells, cathodes, anodes and diaphragms used for the selected technologies are summarized. Based on the cell dimensions, the productivities per unit of cell floor area and of cell volume have been calculated for the USBM, Alcoa and Minemet processes and are listed in Table 20. These data indicate that the fused salt cells have higher productivity than the aqueous electrolysis cell of Minemet.

TABLE 19 - TYPICAL CELL CONFIGURATIONS FOR SELECTED LEAD CHLORIDE ELECTROLYSIS TECHNOLOGIES

	FUSED SALT ELECTROLYSIS					AQUEOUS		RELATED TECHNOLOGIES
	U.S.B.M	ASP	HAZEN/CYMET	ST. JOE	HAZEN/ST. JOE	MINEMET	USBM/HAZEN	BOLIDEN/DEXTEC
CELL								
Configuration	Rectangular, Monopolar	Rectangular, Bipolar	Rectangular, Monopolar	Rectangular, Monopolar	Rectangular, Monopolar	Rectangular, Monopolar	Rectangular, Bipolar	Radial, Monopolar
Inside Dimensions, (L x W x D) cm	86x64x46	191x20x279	46x39x39	264x48x259	-	440x60x300	305x244	300 dia x 300
Outside Dimensions, (L x W x D) cm	135x112x76	245x74x354	48x41x50	297x81x305	396x174x101	-	-	320 dia x 400
CATHODE								
Type	Graphite	Graphite	Graphite	Graphite	Rammed Carbon Paste	Titanium	Graphite	Coppertube, teflon casing
Arrangement	Horiz.Plate or Sawtooth	Horizontal	Vertical Casing	Vertical	Horizontal "V" Casing	Vertical, Plate	30° Inclined, Plate	Vertical
Size (L x W x T) cm	74x60x5	-	-	122x244x10	-	150x60x3.5	-	2 dia x 136-156
Per Cell	1	-	-	1	4	6	6	6x36
ANODE								
Type	Graphite	Graphite	Graphite	Graphite	Graphite	DSA	Graphite	Graphite
Arrangement	Horiz.Plate or Sawtooth	Horizontal	Vertical	Vertical	Vertical V	Vertical Plate	30° Inclined, Plate	Vertical Plate
Size (L x W x T) cm	60x30x7.6	-	-	122x244x10	-	150x60x4	-	176x46x2
Per Cell	2 or 1	-	-	2	8	4	6	36
DIAPHRAGM								
Type	-	-	-	-	-	Rigid-Plastic Frame	-	Non-woven polypropylene

TABLE 20 - COMPARISON OF USBM, ALCOA AND MINEMET ELECTROLYSIS PROCESSES FOR THE PRODUCTION OF LEAD

Process	Cell Floor Area, m^2	Cell Volume, m^3	Productivity per unit area $kg/m^2/h$	Productivity per unit volume $kg/m^3/h$
1. Molten salt electrolysis				
USBM	1.51	1.15	7.3	9.6
Alcoa	1.81	6.42	42.5	12.0
2. Aqueous electrolysis				
Minemet Recherche	2.64	7.92	5.7	1.9

4.3 Comparison of Fused Salt Electrolysis with Aqueous Electrolysis (Cont'd)

This is an indication that the building requirement would be less with the fused salt electrolysis process and therefore, the capital investment required might also be less.

The considerably higher productivity noted for the Alcoa cell design is evidence of an advantage in operating with bipolar electrodes. However, this advantage has to be weighed against the higher energy requirement per unit weight of lead production compared with that of the USBM cell design, namely 1.1 kwh/kg Pb and 0.66 kwh/kg Pb, respectively.

With the available data, it is not possible at this stage to make accurate predictions concerning electrode life, or electrolyte replacement and purification requirements. However, as listed in Table 19, the electrodes required for the USBM cell are smaller than the electrodes required for the Minemet cell (101). This again would indicate a lower capital and operating cost requirement with the USBM cell.

The electrolyte mix used in the USBM cell contained LiCl which is a relatively expensive material, while the Minemet process requires only NaCl (Table 21). However, Alcoa has shown that addition of LiCl to the electrolyte to increase the conductivity and reduce power consumption does not enhance the economics significantly. Therefore, this point should be clarified with further work.

The Minemet process offers options to operate with or without lead chloride crystallization and, during the electrolysis, with chlorine production or without chlorine production together with reoxidation of ferrous to ferric chloride depending on the impurity levels in the concentrate. Operating without a requirement for lead chloride crystallization, and not producing chlorine gas, would provide an advantage over fused salt electrolysis. Even though lead chloride crystallization and chlorine recovery from the fused salt electrolytic cells are straightforward, equipment and labour are required which would add to the investment and operating costs.

As stated earlier, the technical feasibility of the USBM, Alcoa and Minemet processes has been proven and all are applicable to the ferric chloride leach process developed by CANMET. Based on the power requirement and the size of the cell required, the USBM technology has a favourable economic edge compared to the Minemet process while the Minemet process offers a similar advantage with having the option of operating without lead chloride crystallization and chlorine handling.

TABLE 21 - TYPICAL FEED MIX AND PRODUCT HANDLING FOR SELECTED LEAD CHLORIDE ELECTROLYSIS TECHNOLOGIES

TECHNOLOGY	FEED MIX	PHYSICAL STATE[1].	PRODUCT HANDLING
FUSED SALT ELECTROLYSIS:			
USBM	77% $PbCl_2$, 16.5% KCl, 6.5% LiCl	Solid	Siphon/Casting
ASP	15-40% $PbCl_2$, KCl/LiCl = 1.4	Solid	Siphon/Casting
St. Joe	45% $PbCl_2$, 32% KCl, 23% LiCl	Solid	Tapping/Casting
Hazen/Cymet	90% PbCl, 10% NaCl	Molten	Tapping/Casting
Hazen/St. Joe	92% $PbCl_2$, 8% NaCl	Molten	Tapping/Casting
AQUEOUS ELECTROLYSIS:			
Minemet	20 g/l Pb^{2+}, 250 g/l NaCl	Solution	Sponge/Ejector/Compactor/Melting
USBM/Hazen	95% $PbCl_2$, 5% NaCl	Solution	Gravity Separation/Melting
RELATED TECHNOLOGIES:			
Boliden/Dextec	20 g/l Pb^{2+}, 250 g/l NaCl	Solution	Siphon/Wash/Compactor/Melting

[1]. At the time the electrolyte and/or $PbCl_2$ are being fed to the cell.

5.0 CONCEPTUAL DESIGN OF A CELL

5.0 CONCEPTUAL DESIGN OF A CELL

5.1 General

A conceptual design of a fused salt electrolysis cell to produce molten lead from lead chloride crystals has been prepared. The objective was to establish the size and the operating parameters for a pilot plant scale cell that could be used to develop process information having a higher confidence level than that of currently available information. This would facilitate the design of commercial scale cells.

5.2 Options for the Conceptual Cell Design

As a result of the review of existing and emerging metals chloride electrolyis technologies, and the comparison of fused salt electrolysis and aqueous electrolysis, it was possible to identify alternative approaches to the design of a pilot plant scale electrolysis cell.

Three approaches were identified:

I Develop a completely new cell design,

II Select superior features of the technologies developed by two or three companies, and incorporate these features into a new cell design,

III Select a cell design developed by others.

The consequences of taking each of these options were considered as outlined below:

For Option I, the development of a new cell design would be relatively costly and would require a considerable amount of time. The new design could generate technical uncertainties which could require the intermediate stage of laboratory scale test work before a pilot plant could be built.

In carrying out Option II, the incorporation of technologies and know-how of two or three companies could create complicated and costly licencing procedures. In addition, some companies may not be interested in working with their competitors. As in the case of Option I, this approach would also require a relatively long time to finalize the cell design, and this new design could also create technical uncertainties requiring intermediate test work.

5.2 Options for the Conceptual Cell Design (Cont'd)

However, Option II would have the potential advantage of gaining know-how and expertise from two or three sources and having the possibility of selecting the best features of two or three designs. For this approach, a combination of the Minemet Recherche Process, the Clear Process and the Boliden/Dextec Electrowinning Cell could be considered for aqueous electrolysis. For fused salt electrolysis, a combination of the USBM Molten Salt Electrolysis Process and the Alcoa Smelting Process could be considered.

In Option III, the selection of one process and making a licencing agreement with one company would provide the possibility of implementing the pilot plant test program immediately. Compared with the other two options this approach would have relatively less technical uncertainty and would involve only one licence arrangement. It also retains the possibility of gaining some know-how and expertise on the subject from another source. For this approach, the USBM Molten Salt Electrolysis Process, the Alcoa Smelting Process and the Minemet Recherche Process were selected as the best candidates.

Based on the information compiled in the review of the metals chloride electrolysis technologies, and in view of the considerations listed above, Option III was selected as the best approach to take. Among the cell designs, the USBM design was selected as the basis for preparing the conceptual cell design for a pilot scale test program. In addition to the technical considerations, a further factor in this selection was the belief that exchange of information between the government sponsored USBM and Canmet organizations would be simple, and that no licensing fees would be involved. A block diagram illustrating the processing route is included in Figure 16.

5.3 Conceptual Design of a Cell

The conceptual design of the cell is based on a 10,000 A current, and operating parameters similar to those listed in Table 2 for the flat plate electrodes. The USBM cell was designed to operate at a range of 3,000 to 5,000 A current, and it was generally operated at 3,000 A. For a new pilot plant scale electrolytic cell design, a scale up factor of at least 3 or 4 times is believed to be essential. Building a cell to operate at 3,000 A current or less will merely be a duplication of the work already carried out, and would produce data similar to those already published. Accordingly a 10,000 A cell is proposed, which will also reduce the scale up factor to only 4 to 6 times in designing a commercial scale cell, assuming such a cell to be in the range of 40,000 to 60,000 A.

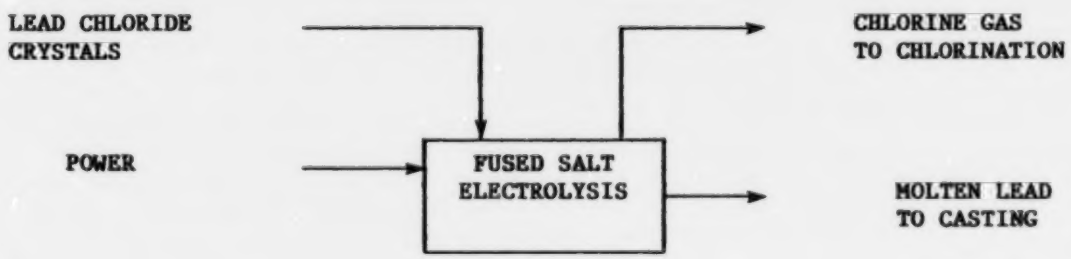


FIGURE 16 - BLOCK FLOW DIAGRAM FOR THE CONCEPTUAL CELL DESIGN

5.3 Conceptual Design of a Cell (Cont'd)

The physical dimensions of the cell are based on a current density of 0.7 A/cm^2 and an electrode spacing of 19 mm or less. The operating parameters of the conceptual cell design are listed in Table 22 while the dimensions for the major components, and other design parameters are listed in Table 23. The cell configuaration is illustrated in Figures 17 through 20.

In preparation of the conceptual cell design, the USBM cell design was studied in detail and consideration was given to items such as electrical operating parameters, mechanical arrangement, materials of construction, electrode and bus bar configurations, the method of lead and chlorine removal, the method of feeding lead chloride crystals, the level of molten lead and electrolyte in the cell, and the production and feed rates. However, a detailed heat balance, load/stress analysis of the components, optimization of design and operating parameters, and cost analysis were not carried out since they are beyond the scope of this study.

The predicted operating parameters with the sawtooth electrodes are also listed in Table 22. It will be possible to replace the flat plate electrodes with the sawtooth electrodes to obtain comparative data and develop the design of the optimum electrode configuration. In the case of sawtooth electrodes, investigation is required to finalize the pitch and depth of the teeth, the number of holes required on the anodes, the cost of electrode production, and their durability.

5.4 Guidelines for Future Work

5.4.1 Economics of Lead Chloride Electrolysis

One of the important conclusions of the review of lead chloride electrolysis technologies is that the economic competitiveness of such electrolysis with existing pyrometallurgical processes has not yet been proven. In addition, there is no published, detailed, cost comparison between lead chloride electrolysis technologies such as the USBM Process, the Alcoa Smelting Process and the Minemet Recherche Process. In view of this, before a commitment is made for a major pilot plant test program, it is believed that a detailed cost comparison of these three processes and a cost comparison with pyrometallurgical processes, should be carried out.

TABLE 22 - OPERATING CONDITIONS FOR A 10,000 A CELL PRODUCING LEAD, WITH EITHER FLAT PLATE OR SAWTOOTH ELECTRODES[1].

	FLAT PLATE	SAWTOOTH
Current, A	10,000	10,000
Voltage, V	4.7	2.5
Electrolyte temperature, °C	450-500	450-500
Electrode current density, A/cm^2	0.7	0.4
Electrode spacing, cm	1.9	1.3
Current efficiency, %	+90	+95
Energy requirement, kWh/kg Pb	1.3-1.5	0.7-0.8
Lead Chloride Feeding Rate, kg/h	47	51
Lead Production Rate, kg/h	35	38
Chlorine Production Rate, l/min. (at 500°C)	164	178
Molten Lead Depth[2], cm (min)	2	2
(max)	6	6
Weight, kg (min)	365	365
(max)	1,094	1,094
Electrolyte Composition[2], wt%	77 $PbCl_2$ + 16.5 KCl + 6.5 LiCl	
Depth, cm (min)	56	56
(max)	60	60
Weight, kg[3] (min)	2,737	-
(max)	3,066	-

1. A conceptual design prepared by SNC on the basis of USBM cell design (Table 2).

2. Lead density at melting point: 10.65 g/cm^3, Electrolyte density at 450-500°C: 4.8 g/cm^3.

3. Not calculated for sawtooth, however, it will be of the same order as for flat plate electrodes.

TABLE 23 - DESIGN PARAMETERS FOR A 10,000 A CELL

Cell Dimensions, inside	153 cm long, 116 cm wide, 77 cm deep
outside	213 cm long, 176 cm wide, 117 cm high
Cell Shell	2 cm steel
Refractory layers, side walls	13 cm - insulating brick 5 cm - castable refractory 10 cm - silica brick
bottom	15 cm - insulating brick 11 cm - silica brick
lid	10 cm - castable insulation
Chlorine exit	4 locations - 6 cm dia. 60 cm high from the top of cell
Lead chloride feeding ports	4 locations - 10 cm dia. 65 cm high from the top of cell
Molten lead siphon holes	2 locations - 5 cm dia. 25 cm high from the top of cell
Bus bars, anode	2 cm x 12 cm copper per anode rod 6 lines for the cell
anode bar contact	12 cm x 12 cm per anode rod
cathode	5 cm x 20 cm steel 2 lines for the cell
cathode bar contact	20 cm x 153 cm per cathode bar
Electrodes, anodes	43 cm x 108 cm x 15 cm 3 graphite anodes per cell 2 cm space in between anodes
anode rods	20 cm dia. x 104 cm high 2 graphite rods per anode
anode rod insulators	25 cm dia. (inside) x 40.1 cm high 21 cm dia. (outside)x 40.1 cm high 1 mullite sleeve per rod
Electrodes, cathodes	133 cm x 108 cm x 10 cm 1 graphite cathode per cell
cathode supports	10 cm dia. x 10 cm high 8 graphite supports per cell
Electrode spacers	5 cm dia. x 1.9 cm high 4 oxy-nitrate spacers per anode 12 spacers per cell

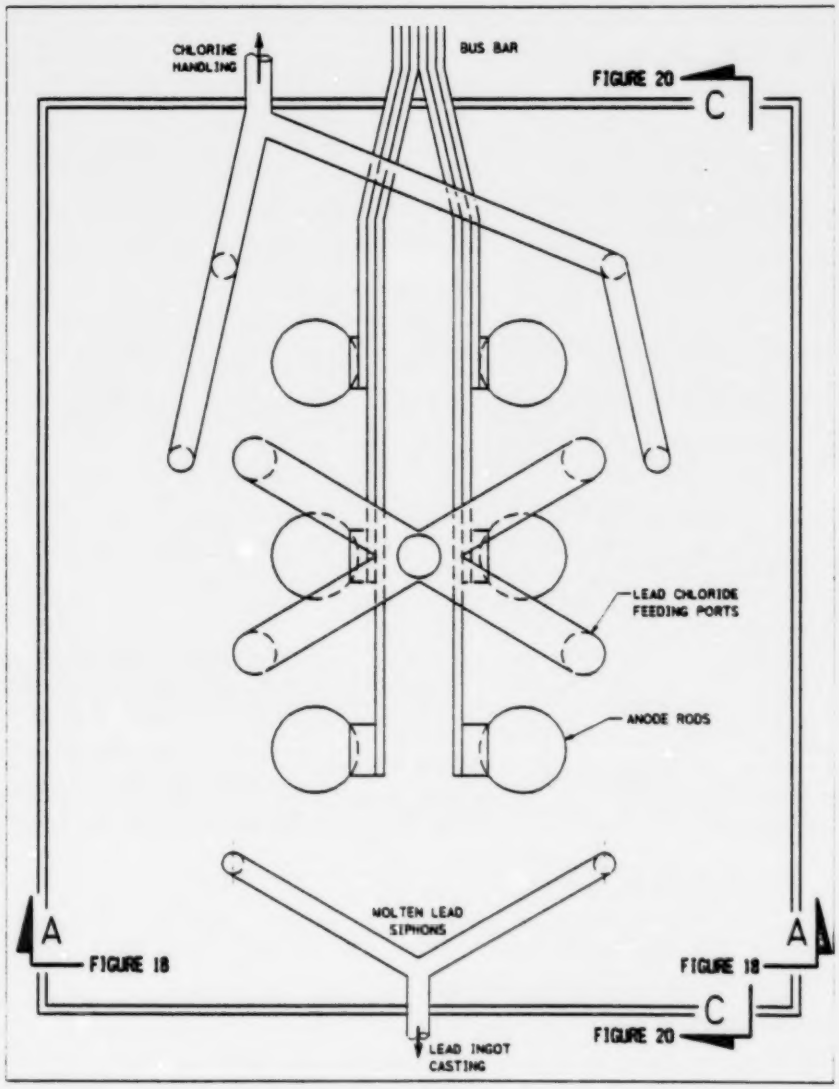


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FIGURE 17 CONCEPTUAL CELL DESIGN
PLAN VIEW

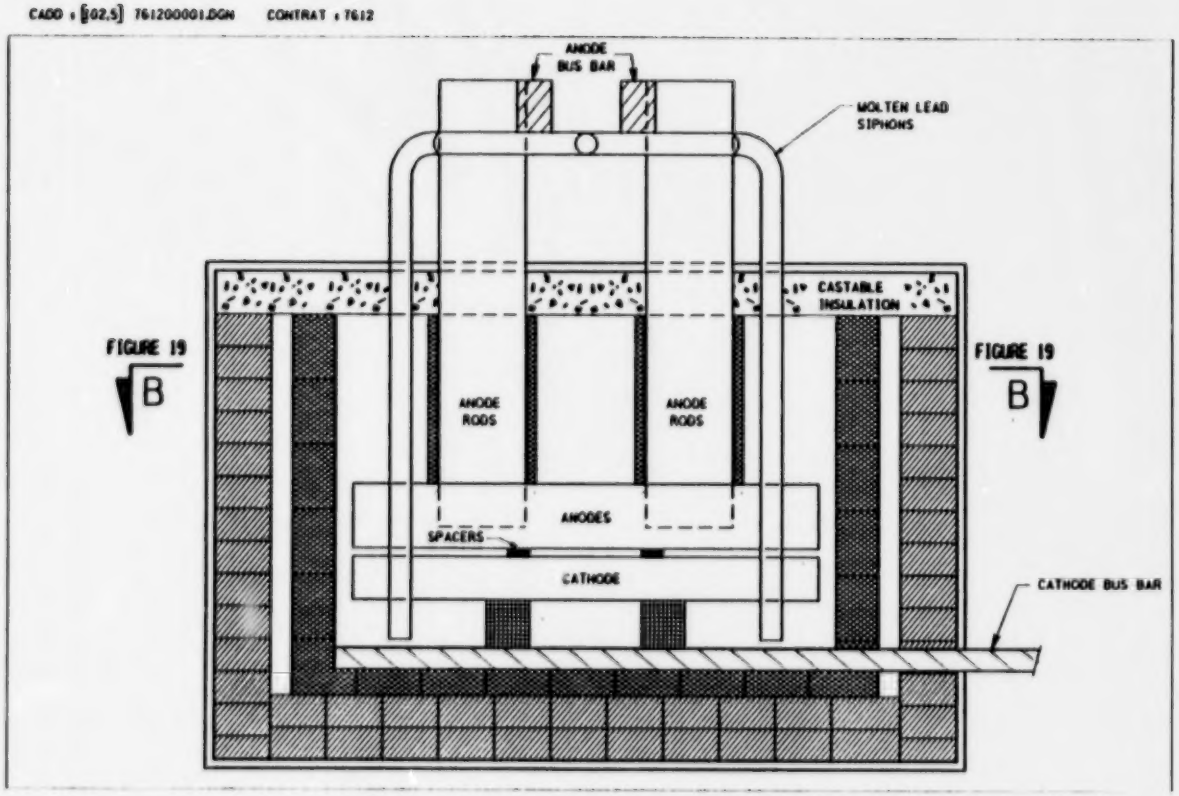

FIGURE 18 CONCEPTUAL CELL DESIGN
SECTION A-A

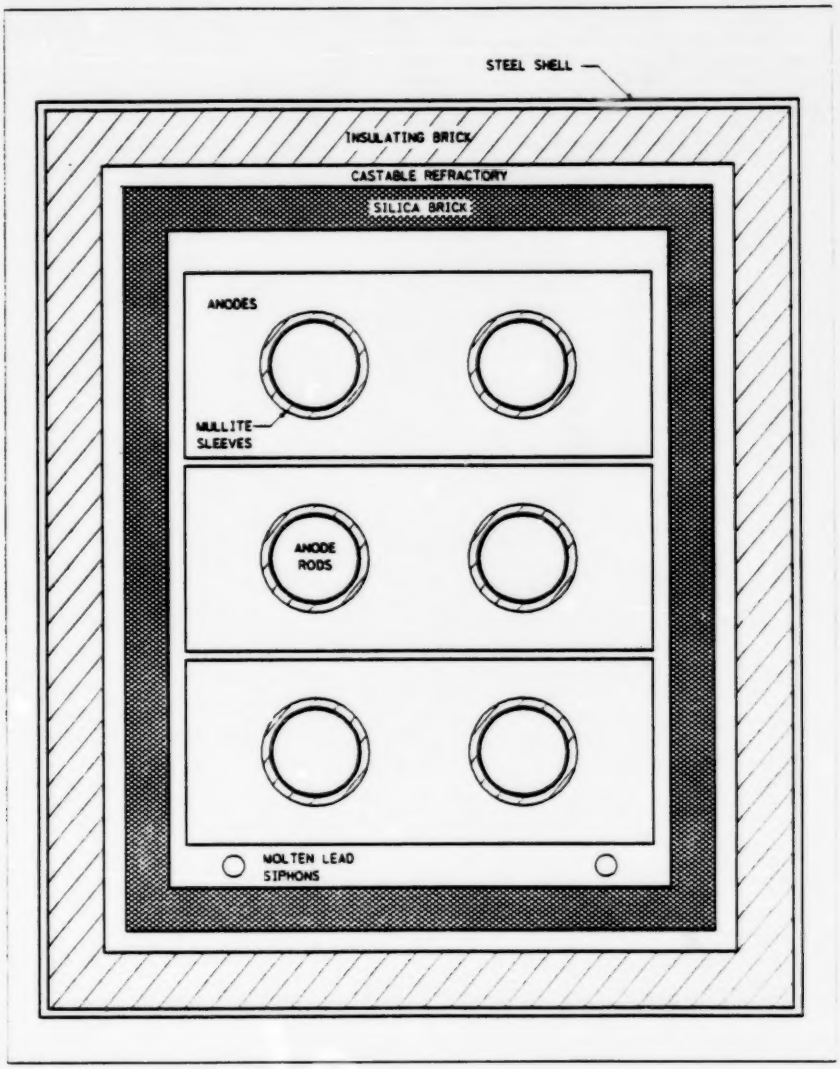

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FIGURE 19 CONCEPTUAL CELL DESIGN
SECTION B-B AT 930mm FROM BOTTOM

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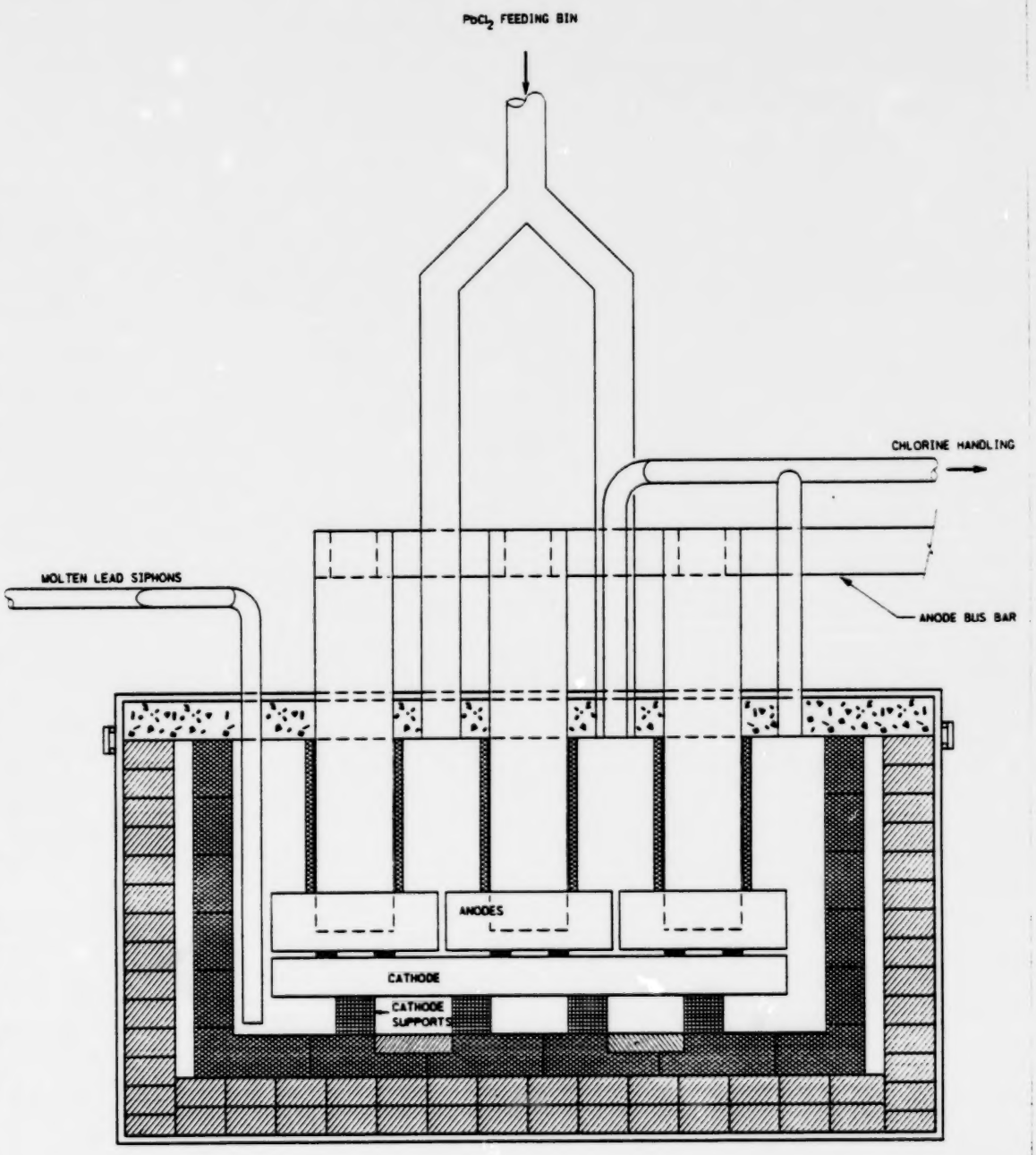

FIGURE 20 CONCEPTUAL CELL DESIGN
SECTION C-C

5.4.1 Economics of Lead Chloride Electrolysis (Cont'd)

These comparisons should be done, at a preliminary engineering cost estimate level, for production of lead from different grades of lead sulphide concentrates through chloride leach and electrolysis, at varying levels of commercial scale production. In general, the economics of the processes vary for different grades of concentrates as well as for different levels of production. For a lead sulphide concentrate and a complex sulphide concentrate, typical compositions can be selected for the process design, while for the significantly different levels of production rate 30,000 and 100,000 tonnes of lead per year can be used as the basis for the capital and operating cost estimates.

This approach is illustrated in the following cost analysis matrix:

PROCESSES	CONCENTRATES			
	LEAD CONCENTRATE		COMPLEX SULPHIDE CONCENTRATE	
	LEAD PRODUCTION RATE x 1000 t/y			
	30	100	30	100
USBM Process				
Alcoa Smelting Process				
Minemet Recherche Process				
Selected Pyrometallurgical Process - I				
Selected Pyrometallurgical Process - II				

It is believed that this approach would provide sufficient data to enable CANMET to select the electrolysis technology for the pilot plant scale test program more accurately.

5.4.2 CANMET Ferric Chloride Leach-Electrolysis Process Flowsheet

At the progress review meeting held on February 13, 1987 with the Scientific Authority, it was stated that recently certain modifications had been made to the ferric chloride leach process being developed by CANMET. With these modifications, the process would be able to treat complex sulphide concentrates, lead containing

5.4.2 CANMET Ferric Chloride Leach-Electrolysis Process Flowsheet (Cont'd)

dusts and lead dross, and to remove lead from copper concentrates, as well as treating lead sulphide concentrates. However, it was noted that these modifications are still in the development stage and work is continuing to finalize the operating parameters of the unit processes.

In view of this development, it is believed that for the near future the best approach would be to set up a laboratory scale test program to run the entire flowsheet continuously for reasonably long periods in an integrated mode including a small fused salt electrolysis cell compatible with the other unit processes. If, due to the number of unit processes involved in the flowsheet, this is not practical, then the flowsheet should be divided into reasonably independent circuits and each circuit should be operated continuously to prove the technical feasibility of the process.

While this work is continuing, simultaneously the cost analysis of the lead chloride electrolysis processes can be carried out and when the results of both investigations are available a decision can be made for the pilot plant scale test program.

5.4.3 Pilot Scale Test Program

During the review of fused salt and aqueous electrolysis technologies, it has become evident that certain operating parameters are still not firmly established. If a pilot plant scale test program is to be initiated with a 10,000 A cell in the future, the following parameters are identified to be given priority:

- Anode and cathode wear rate,
- Cell refractory wear rate,
- Electrolyte replacement and purification requirements,
- Electrolyte composition, with particular reference to elimination of LiCl,
- Cell heating characteristics and heat losses,
- Effects on voltage drop and its measurement, of anode type, cathode type, electrode spacing, bus bar configuration, electrolyte composition, cell temperture and lead chloride decomposition,
- Selection of materials of construction,
- Optimization of cell size,
- Optimization of electrode configuration,
- Optimization of sizes of major components,
- Further optimization of current density.

5.4.4 Chloride Metallurgy

This study has shown that over the last two decades, treatment of base metal sulphide concentrates in a chloride medium has been established as a technically viable alternative to existing pyrometallurgical processes. The existing pyrometallurgical processes face two major problems, first, the high cost of containment of sulphur dioxide, and second, inefficiency in treating complex base metal sulphide concentrates. Until these problems are resolved, chloride metallurgy will remain to be an important alternative. With the developments taking place in this field, even after the above mentioned problems of the pyrometallurgical processes are solved, chloride metallurgy may become a preferred process for the production of lead, zinc, silver and copper as it is the commonly used process to produce magnesium, titanium and nickel. It is believed that CANMET should continue its involvement in this field.

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

- The technical feasibility of the production of lead from lead chloride crystals or solution, by fused salt or aqueous electrolysis, has been proven in pilot plant operations. After a test program with a prototype cell, it would be possible to build commercial scale plants.

- The purity of the lead produced is dependent on the purity of the lead chloride, in both fused salt and aqueous electrolysis, and the crystallization stage is the key to the production of high purity lead chloride.

- The USBM Molten Salt Electrolysis Process and the Alcoa Smelting Process have been identified as the most advanced fused salt electrolysis technologies.

- The Minemet Recherche Process and the Boliden/Dextec Electrowinning Cell have been identified as the most advanced aqueous electrolysis technologies.

- The Boliden/Dextec Electrowinning Cell technology is not directly applicable to the ferric chloride leach-electrolysis approach of CANMET since leaching and electrolysis of the sulphide concentrates take place in one electrolytic cell.

- The economic competitiveness of lead chloride electrolysis with existing pyrometallurgical processes has not been proven. Similarly, a comparative economic evaluation of the USBM process, the Alcoa Smelting Process and the Minemet Recherche Process is not available. Not having these data makes a confident selection of a technology to be adopted for a pilot scale test program difficult.

- The USBM process has a favourable economic edge compared to the Minemet Recherche Process, based on the data available from the pilot plant operations.

- For the development of the conceptual design of a cell a 10,000 A current has been selected as the basis.

6.2 Recommendations

- For the near future, it would be best to set up a laboratory scale test program to prove the technical feasibility of the entire two-stage ferric chloride leaching process flowsheet of CANMET.

- Before a commitment is made for a pilot scale test program, a cost comparison of the USBM process, the Alcoa Smelting Porcess and the Minemet Recherche Process, and a comparison of these processes with existing lead producing pyrometallurgical processes should be carried out.

- In setting up a pilot scale testing facility, the best approach would be to adopt one of the cell technologies developed by others. The USBM process appears to be the best option for this purpose.

- It is believed that CANMET should continue its involvement in the field of production of base metals from sulphide concentrates by use of a chloride medium.

7.0 ACKNOWLEDGEMENTS

7.0 ACKNOWLEDGEMENTS

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Report reviewed by: F. Wright/P.D. Kermack/R. Minto

8.0 REFERENCES ON LEAD CHLORIDE METALLURGY PUBLISHED IN ENGLISH OR FRENCH

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